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ON THE SPECIFIC GRAVITIES OF MIXTURES OF NORMAL LIQUIDS.

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I.

The molecular masses of substances being established by getting them into the gaseous or dissolved state and then comparing their density or concentration in the light of the hypotheses of Avogadro and van't Hoff, with that of a standard substance, it is not allowable without experimentation along other lines to affirm that the molecular mass of a liquid or solid is the same as that it possesses when vaporized. When a gas is condensed into a liquid, or the solvent is removed from a dissolved substance which we assume to be liquid, it is conceivable that the pure liquid may have a greater, the same, or a smaller molecular mass than it does in the gaseous or dissolved state; it may be made up of "associated," "normal," or "dissociated" molecules.

Now, all experimental evidence indicates that substances in the gaseous state present the simplest phenomena and relationships; also, high temperatures necessary for the maintenance of the vaporous state are inimical to molecular complexity. It may be conceded then that the molecular condition of a substance in the gaseous state is simpler than in the liquid state, and that no dissociation occurs when a gas, made up of

molecules remaining of the same size throughout considerable ranges of temperature, condenses into a liquid.

But can vapors on condensing to liquids preserve their molecular size unaltered? And is the difference between the gaseous and liquid state to be alone attributed to a difference between the mutual attractions of the molecules? The work of Guye, Ramsay and Shields, and others, interpreted as it has been, indicates that these questions can often be answered in the affirmative; there exist many compounds which suffer no change in molecular condition in passing from the one state of aggregation into the other; the number of "normal liquids" is legion.

But there also exist numerous compounds which undergo more or less radical changes in passing from the one state of aggregation into the other. There are some—the alcohols, for example—which possessing normal molecules in the gaseous state suffer polymerization on liquifying; and there are others, for instance, the acids, that made up even in the gaseous state of polymerized molecules, experience comparatively slight changes in their degree of polymerization on assuming the liquid state.

Now, it happens that the more commonly occurring liquids are those which exhibit an intricate molecular structure, and, in the investigations of the properties of liquids, such have naturally enough been employed. But, their molecular structure being so complex, it is no wonder that so few general results have been obtained, for an associated liquid cannot be considered as a type, and all determinations of its behavior in the pure or mixed state are merely individual and cannot be taken as characteristic of the liquid state in general. If, however, the disturbing factor of molecular complexity be removed, and "normal liquids" be investigated, it is legitimate to expect more uniformity and generality of results, and the examination of a few simple liquids may give us a comprehensive insight into the nature of liquid structure.

Among the important physical properties of liquids is that of volume, and, although much has been done on the subject, much remains to be done. Such questions as these arise: What changes of volume occur when liquids are mixed? Will

the mixing of normal liquids be accompanied with an increase or decrease of volume, or will it, since no change in the number of molecules occurs, occasion no change of volume? Does the contraction or expansion that may supervene depend upon the chemical characteristics or the physical properties of the normal liquids mixed?

The object of this paper is to attempt a partial theoretical and experimental elucidation of these and kindred questions.

II.

Historical and Critical.

If the degree of molecular association of liquids be taken as a basis of classification, three classes of binary mixtures may be distinguished.

1. The liquids mixed are normal;
2. One liquid is normal, the other associated;
3. Both liquids are associated.

Of course, there is nothing fixed or absolute in these classes, since there may occur every degree of association in liquids from carbon bisulphide in which it is hardly detectable even at low temperatures to sulphuric acid which has been found probably to consist of more than thirty simple molecules. Still it is convenient for reference and discussion to make such a classification.

Without doubt, the mixtures of the first class may be expected to exhibit the simplest behavior in respect to their physical properties, and, indeed, all determinations of density which have been made upon mixtures of normal liquids have shown such to be the case. Thus, Bussy and Buignet[1] in the course of their investigations on the change of temperature brought about by the mixing of liquids determined the changes of volume occurring from the mixing. In the absence of any experimental particulars, it is impossible to judge of the accuracy of their determinations or of the purity of the liquids employed. Only two mixtures of normal liquids (and one of these, carbon bisulphide, is slightly associated) were examined, about which the authors write the following:

[1] Bussy and Buignet; Recherches sur les changements de temperature produits par le mélange des liquides de nature differente. Comptes rendus. **59**, 671 (1864); and Annales de chimie et de physique (4 ser.) **4**, 5 (1865).

"*Ether et sulfure de carbone*—Le changement de volume qui accompagne le mélange de ces deux liquides est très-peu marqué. Il consiste en une contraction qui, pour le mélange ou elle atteint un maximum, n'excède guere 2 millièmes de volume théorique total."

"*Chloroforme et sulfure de carbone*—Le mélange de ces deux liquides donne toujours lieu à une augmentation de volume. .....Le maximum correspond au mélange formé par 3 équivalents de sulfure de carbone pour en seul équivalent de chloroforme ; il represente un peu plus des 6 milliemes du volume théorique total."

Also, Frederick D. Brown[1] has very carefully determined at temperatures in the vicinity of 20° the densities of mixtures of carbon bisulphide with carbon tetrachloride, of benzene with dichlorethane, dibromethane, and carbon tetrachloride, and of toluene and carbon tetrachloride, all except carbon bisulphide being normal liquids. The volume relations of these mixtures to their components were found to be very simple in comparison with those obtained with mixtures containing associated liquids. His data, which may be regarded as very accurate, will be reproduced and discussed later on.

Recently, E. Paternò and C. Montemartini[2] have determined the densities at 20° of mixtures of benzene with methyl, ethyl, isopropyl, isobutyl, and caproic alcohol ; with acetic and isobutyric acids, and anethol. All of these liquids, with the exception of benzene, are more or less associated ; the mixtures, accordingly, belong to the second of the classes mentioned above, and, as might be expected, more deviation from simplicity is to be found in their determinations than in those made by Brown.

A number of isolated determinations of the densities of mixtures of liquids of the second class might be cited, but it is unnecessary, as they are for the most part of doubtful accuracy and are outside of the domain of our subject.

When we consider mixtures of the third class, we find the

[1] On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride : Transactions of the Chemical Society, **39**, 304 (1881).

[2] Sulle variazioni di volume nei miscugli dei liquide in relazione al comportamente crioscopico. Gazzetta chimica italiana. Vol. II, anno XXIV, 179-190 (1894).

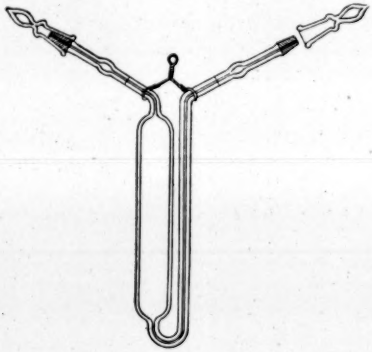
differences between the densities calculated by the rule of mixtures, and those determined by direct experiment to be considerably greater than those found in the previous two classes. The possibility of ascertaining the composition of mixtures of liquids of commercial importance, as of water and alcohol, water and acids, etc., etc., most of which are associated liquids, by means of a determination of their specific gravities, an operation of great simplicity, especially if the convenient hydrometer be used, and yet of considerable accuracy, has led to the investigation of the densities of mixtures of a number of such liquids. But the volume relations of these mixtures exhibit many irregularities, due, no doubt, to the amount of association becoming altered through the mixing. For illustration, in every one of the possible mixtures of ethyl alcohol and water, there must be a definite number of simple and a definite number of associated molecules, of the latter of which there may be several different kinds. The decomposition of the complex molecules brought about by the successive addition of either constituent to any mixture may be continuous or possibly discontinuous, and for certain mixtures there may be maxima or minima of density. When such mixtures possess an approximately simple stoichiometrical composition, it has been claimed that definite molecular compounds have been formed, the so-called "hydrates." But it is remarkable that only such liquids as possess a considerable complexity of molecular structure have a tendency towards the formation of "hydrates" and it seems probable that this very intricacy of structure is the cause of the "breaks" in the continuity of the curves representing the relation between specific gravity and composition, and that it is only pure accident that such "breaks" occur at points, which, by a liberal allowance for experimental errors, may be regarded as integral stoichiometrical ratios, and so indicating the presence of "hydrates." Also, it is an experimental fact that the number and position of these breaks varies with the temperature; the higher the temperature, the less pronounced and distinct the "hydrates." This fact, which has been speciously claimed to be due to the breaking up of "hydrates" under the influence of heat, more rationally can be

said to be due to the decomposition of the more complex into simpler molecules through rise of temperature; and the simpler the molecules, the simpler the relationships.

III.

Experimental Details.

For the determination of the specific gravities of the liquids and their mixtures, pycnometers having the form represented in Fig. 1 were employed. Three of them were used, having



capacities of about 15 cc., 25 cc., and 40 cc., respectively. Every precaution was taken to prevent any alteration in their capacity. They were never exposed to temperatures far removed from 25°, the temperature at which the determinations were made, for it is a well established fact that glass vessels, when subjected to considerable changes of temperature, suffer temporary and even permanent changes of capacity. Their content of water was often determined during the course of the investigation, but its variation was never found to be greater than that due to unavoidable experimental errors, so that their capacity may be said to have remained unchanged. A slight loss was found to have occurred in the weight of the empty pycnometers, due to "wear and tear," probably from the putting on and taking off of the glass caps; this loss,

however, was very slight, amounting, in the case of the pycnometer used the most, to but 0.0013 gram after the performance of more than 100 determinations; as the pycnometers were weighed empty after every dozen or so of experiments, account could be taken of this slight loss.

Plenty of time was always given for the liquid or mixture to acquire the temperature of the bath in which it was immersed; after the weighing of the pycnometer and its contents it was again placed in the bath, and if the liquid did not assume exactly the same volume as at first, the determination was repeated; this was found, however, to be necessary in only a very few cases.

The weighings were carried out with a balance capable of indicating a tenth of a milligram with accuracy, and the same set of weights, which had been carefully tested, was always employed.

The thermostat was an enamelled iron kettle holding about thirty quarts of water. As the temperature of the room in which the experiments were made could be kept within a degree or so of 25°, the water in the bath, which was stirred continuously by an automatic device, could be kept from that temperature by not more than 0°.01 to 0°.02 for an hour or so.

The thermometer used was graduated in tenths of degrees, and permitted of the pretty accurate estimation of fiftieths of degrees; it had been tested by the "Physikalische Reichsanstalt," and had been found to be "ohne merklichen Fehler" from 20°.0 to 30°.0.

Notwithstanding my efforts to push the degree of accuracy in densimetric work as far as possible, I cannot claim that my determinations are accurate to more than a few units of the fifth decimal place; still in many cases there is no doubt that the results are more accurate than this, but, on an average, only the above claim is justifiable.

IV.

Purification of Liquids and Preparation of Mixtures.

Although desirable, it is not absolutely necessary to employ in the investigation of the volume relations of mixtures of

liquids, material that has been subjected to the most careful preparation. The presence of the amount of impurity contained in the preparations furnished by reputable makers as "chemically pure" is of vanishing influence in the results, inasmuch as these are relative and not absolute. Brown (*loc. cit.*) was also of this opinion, being led to it by a consideration of his results obtained with samples of dibromethane of different degrees of purity. The main thing in an investigation of this sort is the accuracy of the experimental work. For example: It was found that a mixture containing 47.322 per cent. of toluene and 52.678 per cent. of ethyl benzoate had a specific gravity of 0.94937, while the specific gravity as calculated by the rule of mixtures, was 0.94806, the difference, accordingly being 0.00131; the specific gravity of the ethyl benzoate contained in this mixture was 1.04843. In another mixture containing 51.249 per cent. of toluene and 48.751 per cent. of another sample of ethyl benzoate, whose specific gravity was 1.05455, a specific gravity of 0.94445 was found, differing by 0.00134 from the calculated specific gravity 0.94311. We have then two mixtures of nearly the same percentage composition having differences of specific gravity measured and calculated, 0.00131 and 0.00134, while the samples of ethyl benzoate employed differed by 0.00612 in their specific gravities. In the data communicated later some similar results may be found.

I have not, accordingly, used in every case liquids of the greatest purity, and, although the employment of material of different degrees of impurity may introduce a little confusion, the certainty of the results is in nowise lessened.

In the following paragraphs are indicated briefly the methods of purification adopted, together with some physical properties of the liquids serving as criteria of their degree of purity.

Benzene I.—About three pounds of benzene, labelled chemically pure and free from thiophene, were treated with sulphuric acid to remove last traces of thiophene; the liquid was then subjected to fractional crystallization until a little over a pound was obtained melting at 5°.3 (uncorr.). The whole was dis-

tilled over a little sodium, most of it boiling at 80°.1 (uncorr.) under a pressure of 756 mm. of mercury.

Benzene II.—About five pounds of "chemically pure" benzene were treated many times with sulphuric acid and crystallized repeatedly. It was then distilled over some pieces of sodium, the whole of it boiling at 80°.12 (corr.) under a pressure of 757.3 mm. of mercury. The distillate was collected in three portions of somewhat more than a pound each, and their melting-points determined by means of a thermometer graduated in hundredths of degrees; these were found to be 5°.39 (corr.), 5°.40 (corr.) and 5°.42 (corr.) This sample can hence be regarded as of a very high degree of purity.

Toluene I.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at 109°.8 to 110°.1 (uncorr.), an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling almost constantly at 110°.1 (uncorr.) under a pressure of 758 mm. of mercury.

Toluene II.—Five pounds of toluene (Merck's chemically pure boiling at 110°–112°) were fractionally distilled a half dozen times or so until the larger portion boiled almost constant. Three fractions of nearly a pound each were taken boiling: *a* at 109°.90–109°.94; *b* at 109°.94–110°.00, and *c* at 110°.00–110°.03 under a pressure of 757.7 mm. The specific gravities at 25°.0 referred to water at the same temperature were: *a* 0.85678; *b* 0.85681, and *c* 0.85680; that is, they were practically the same.

Monochlorbenzene.—A couple of pounds of commercially pure benzene monochloride was fractionally distilled until nearly half of it boiled at 131°.8 to 131°.9 (uncorr.) under a pressure of 757 mm. of mercury.

Nitrobenzene.—The commercial article was repeatedly crystallized in fractions until an almost colorless product was obtained, which when solidified showed the same temperature during the remelting, *viz.*, 3°.6 (uncorr.).

Ethyl Ether.—Five pounds of ordinary ether were washed a couple of dozen times with small portions of water, dried over fused calcium chloride, allowed to stand over mercury

for a few days and finally distilled over sodium. Almost the total quantity distilled within 0°.1 degree. The portion which was found to boil at an almost constant temperature was distilled over phosphoric anhydride, and the distillate collected in two portions. Their specific gravities at 25°.0 referred to water at 25°.0 were found to be 0.70940 and 0.70944, respectively, almost identical results.

Acetic Ether I.—A kilogram of C. P. ethyl acetate was fractionally distilled until about a third of it was found to boil within a few tenths of a degree.

Acetic Ether II.—Five pounds of commercial acetic ether were dried for several days over fused calcium chloride, and after filtration from this salt, were allowed to stand for several days over phosphoric anhydride. It was then distilled, the distillate being collected in two portions, one of which boiled at 71°.0–71°.3 (uncorr.), the other at 71°.3–71°.4 (uncorr.). Each of these distillates was then distilled over about half a pound of phosphoric anhydride, when they were found to boil throughout the distillations at identical temperatures. The specific gravity of one sample at 25° referred to water at the same temperature was determined to be 0.89155; that of the other under similar conditions, 0.89157.

Carbon Bisulphide.—Several different preparations of carbon bisulphide were used in the work, all of which had practically identical properties. The method of purification adopted was distillation over mercury and dehydrated copper sulphate. As this compound decomposes somewhat on exposure to light, it was redistilled before the preparation of each series of mixtures.

Turpentine.—The sample used was kindly furnished me by Prof. J. H. Long, of the Northwestern University, who had had it prepared in his laboratory by the distillation of pure spruce gum. It had been rectified over sodium and boiled at 156°.5–157° (uncorr.) under a pressure of 745 mm. of mercury.

Ethyl Benzoate.—This ester was prepared by the action of hydrochloric acid gas on a mixture of benzoic acid and absolute alcohol in the customary way. It was repeatedly recti-

fied, and two different distillates used: I, boiling at 210°.3–210°.8 (uncorr.), and II, boiling at 210°.8–212°.8 (uncorr.), under a pressure of 758 mm. of mercury.

Ethyl Iodide.—The ethyl iodide was made by the action of iodine and red phosphorus on absolute alcohol, and after a couple of fractional distillations a constant boiling portion was obtained. This portion was again distilled and the distillate collected in two equal portions. The specific gravity of the first portion at 25°.0 referred to water at the same temperature was 1.93012, that of the second under the same conditions was 1.93015.

Chloroform.—The chloroform had been fractionated to constant boiling-point, and was finally distilled over phosphoric anhydride; its boiling-point was 61°.3 (uncorr.) under a pressure of 759 mm. of mercury.

Carbon Tetrachloride.—The sample had been fractionally distilled over phosphoric anhydride, after preliminary treatment with concentrated sulphuric acid, and boiled at 76°.7 (uncorr.) under a pressure of 754 mm. of mercury.

The mixtures were prepared by weighing the liquids to less than half a milligram in a bottle or flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from forty to one hundred grams of the mixture were weighed out, its composition was known to a ten-thousandth, at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and stored in a dry, cool, dark closet. Invariably, their specific gravities were determined immediately after their preparation, although it was found in all the cases that were tried that their specific gravities did not change even when they had been made up for more than a year.

V.

Experimental Results.

In the following tables are recorded the experimental data obtained. In the first two columns are given the composition of the mixtures in percentages; in the third and fourth the composition in molecular percentages. The fifth column

gives the theoretical specific gravities of the mixtures as calculated from those of their component liquids by means of the formula,

$$D = \frac{d d_1 (p + p_1)}{p d_1 + p_1 d},$$

wherein p and p_1 represent the weights of the two liquids, and d and d_1 their respective specific gravities. In the sixth column are placed the specific gravities of the liquids and their mixtures as actually determined. All of the specific gravities are referred to water at the same temperature, no reductions to 4° or a vacuum being made; the data then are quite independent of any reduction formulas or constants, but are simply the direct results of experiment.

In the seventh column, finally, are shown the differences between the observed and calculated values; a plus sign before a number indicates that the observed value is less than the calculated one, while a minus sign shows the opposite. I do not think it necessary to represent the data in a graphical form, as the curves, which I constructed in each case, are remarkably uniform, and the numbers in the seventh column show almost as well as a curve the trend of the phenomena.

It might seem as if it were advisable to communicate the following data in the form of specific volumes as well as specific gravities. The advantage claimed for the first mode being, however, only of algebraical nature, and it being easy enough to obtain specific volumes from the specific gravities, the data for the last were thought sufficient.

TABLE I.

Specific Gravities of Mixtures of Benzene II. and Ethyl Ether.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	$C_4H_{10}O$	C_6H_6	$C_4H_{10}O$			
0.000	100.000	0.000	100.000		0.70942	
28.576	71.424	27.502	72.498	0.74971	0.75369	—0.00398
56.924	43.076	55.627	44.373	0.79455	0.79972	—0.00517
75.691	24.309	74.709	25.291	0.82728	0.83179	—0.00451
100.000	0.000	100.000	0.000		0.87390	

TABLE II.

Specific Gravities of Mixtures of Benzene I. and Acetic Ether II.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	$C_4H_8O_2$	C_6H_6	$C_4H_8O_2$			
0.000	100.000	0.000	100.000		0.89663	
15.594	84.406	17.250	82.750	0.89346	0.89285	+0.00061
51.404	48.596	54.411	45.589	0.88625	0.88506	+0.00116
80.803	19.197	82.605	17.395	0.88038	0.87982	+0.00056
100.000	0.000	100.000	0.000		0.87661	

TABLE III.

Specific Gravities of Mixtures of Benzene I. and Carbon Tetrachloride.

Temperature, 20°.0 (Brown).

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	CCl_4	C_6H_6	CCl_4			
		0.000	100.000		1.59742	
		10.074	89.926	1.53049	1.53059	—0.00010
		20.363	79.637	1.46099	1.46116	—0.00017
		30.216	69.784	1.39331	1.39363	—0.00032
		40.748	59.252	1.31974	1.32004	—0.00030
		50.422	49.578	1.25101	1.25120	—0.00019
		60.437	39.563	1.17796	1.17825	—0.00029
		70.585	29.415	1.10408	1.10420	—0.00012
		80.533	19.467	1.02971	1.02983	—0.00012
		90.511	9.489	0.95380	0.95388	—0.00008
		100.000	0.000		0.88038	

Temperature, 23°.0 (Linebarger).

0.000	100.000	0.000	100.000		1.59156	
13.728	86.273	23.860	76.140	1.43202	1.43214	—0.00012
40.779	59.221	57.550	42.450	1.19579	1.19598	—0.00019
58.600	41.400	73.599	26.401	1.07861	1.07868	—0.00007
100.000	0.000	100.000	0.000		0.87847	

Temperature, 25°.0 (Linebarger).

0.000	100.000	0.000	100.000		1.58828	
13.727	86.273	23.860	76.140	1.42942	1.42956	—0.00014
40.779	59.221	57.550	42.450	1.19328	1.19339	—0.00011
58.600	41.400	73.599	26.401	1.07632	1.07642	—0.00008
100.000	0.000	100.000	0.000		0.87661	

TABLE IV.

Specific Gravities of Mixtures of Benzene I. and Chloroform.

Temperature, 25.°0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$CHCl_3$.	C_6H_6	$CHCl_3$			
0.000	100.000	0.000	100.000		1.48069	
6.970	93.030	10.291	89.709	1.41613	1.41203	+0.00410
23.011	76.989	31.410	68.590	1.27788	1.27568	+0.00220
72.780	27.220	80.370	19.630	0.98619	0.98485	+0.00134
85.830	14.171	90.289	9.711	0.93042	0.92965	+0.00077
100.000	0.000	100.000	0.000		0.87661	

TABLE V.

Specific Gravities of Mixtures of Benzene I. and Nitrobenzene.

Temperature 25.°0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_6H_5NO_2$.	C_6H_6	$C_6H_5NO_2$.			
0.000	100.000	0.000	100.000		1.20200	
14.394	85.606	20.956	79.044	1.14105	1.14200	—0.00095
37.610	62.390	48.735	51.265	1.05477	1.05620	—0.00143
80.053	19.947	86.355	13.645	0.92664	0.92764	—0.00100
100.000	0.000	100.000	0.000		0.87661	

TABLE VI.

Specific Gravities of Mixtures of Benzene I. and Carbon Bisulphide.

Temperature, 19°.80 (Brown).

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	CS_2.	C_6H_6.	CS_2.			
0.000	100.000	0.000	100.000		1.26642	
5.327	94.673	5.198	94.802	1.23751	1.23459	+0.00292
17.201	82.799	16.835	83.165	1.17758	1.17184	+0.00574
20.195	79.805	19.780	80.220	1.16338	1.15700	+0.00638
27.537	72.463	27.022	72.978	1.12996	1.12241	+0.00755
34.613	65.387	34.027	65.973	1.09952	1.09132	+0.00820
38.980	61.020	38.364	61.636	1.08153	1.07250	+0.00903
49.612	50.388	48.963	51.037	1.04012	1.03126	+0.00886
59.039	40.961	58.409	41.591	1.00596	0.99868	+0.00728
60.581	39.419	59.959	40.041	1.00059	0.99354	+0.00705
75.074	24.926	74.585	25.415	0.95274	0.94744	+0.00530
87.366	12.634	87.077	12.923	0.91561	0.91307	+0.00254
100.000	0.000	100.000	0.000		0.88034	

Temperature, 25°.0 (Linebarger).

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_4H_{10}O$.	C_6H_6.	$C_4H_{10}O$.			
0.000	100.000	0.000	100.000		1.25958	
8.872	91.127	8.675	91.325	1.21257	1.20897	+0.00360
34.858	65.142	34.270	65.730	1.09314	1.08494	+0.00820
75.886	24.114	75.409	24.591	0.94607	0.94176	+0.00431
100.000	0.000	100.000	0.000		0.87661	

Table VII.

Specific Gravities of Mixtures of Benzene I. and Toluene I.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	C_7H_8.	C_6H_6.	C_7H_8.			
0.000	100.000	0.000	100.000		0.86288	
10.990	89.010	12.720	87.280	0.86446	0.86434	+0.00012
30.558	69.412	34.229	65.771	0.86712	0.86635	+0.00072
51.920	48.080	56.020	43.980	0.87002	0.86920	+0.00082
66.433	33.567	70.000	30.000	0.87197	0.87140	+0.00057
66.576	33.424	70.240	29.760	0.87198	0.87143	+0.00055
91.556	8.444	92.750	7.250	0.87549	0.87528	+0.00021
100.000	0.000	100.000	0.000		0.87661	

Table VIII.

Specific Gravities of Toluene II. and Turpentine.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_{10}H_{16}$.	C_7H_8.	$C_{10}H_{16}$			
0.000	100.000	0.000	100.000		0.85970	
6.791	93.209	9.724	90.276	0.85955	0.85948	+0.00007
20.654	79.346	24.464	72.536	0.85910	0.85838	+0.00072
53.701	46.299	63.162	36.838	0.85815	0.85682	+0.00133
75.091	24.909	89.884	20.116	0.85801	0.85654	+0.00147
100.000	0.000	100.000	0.000		0.85680	

Table IX.

Specific Gravities of Mixtures of Toluene II. and Ethyl Benzoate I.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_9H_{10}O_2$.	C_7H_8.	$C_9H_{10}O_2$.			
0.000	100.000	0.000	100.000		1.04843	
15.282	84.718	22.726	77.274	1.01378	1.01458	—0.00080
47.322	52.678	59.450	40.550	0.94806	0.94937	—0.00139
76.170	23.830	83.918	16.082	0.89580	0.89667	—0.00087
100.000	0.000	100.000	0.000		0.85680	

Specific Gravities of Mixtures of Toluene II. and Ethyl Benzoate II.

0.000	100.000	0.000	100.000		1.05455	
51.249	48.751	63.152	36.848	0.94311	0.94445	—0.00136
100.000	0.000	100.000	0.009		0.85680	

TABLE X.

Specific Gravities of Mixtures of Toluene I. and Nitrobenzene.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_6H_5NO_2$.	C_7H_8.	$C_6H_5NO_2$.			
0.000	100.000	0.000	100.000		1.20200	
15.400	84.600	19.566	80.434	1.13334	1.13523	—0.00189
37.410	62.590	44.406	55.594	1.04795	1.05084	—0.00289
70.957	29.043	76.554	23.446	0.93991	0.94240	—0.00249
87.796	12.204	90.579	9.421	0.89365	0.89478	—0.00143
100.000	0.000	100.000	0.000		0.86288	

TABLE XI.

Specific Gravities of Mixtures of Toluene I. and Monochlorbenzene.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	C_6H_5Cl.	C_7H_8.	C_6H_5Cl.			
0.000	100.000	0.000	100.000		1.10362	
19.756	80.244	23.290	76.710	1.04704	1.04768	—0.00064
53.364	46.636	58.181	41.819	0.96061	0.96159	—0.00098
77.713	22.287	81.010	18.990	0.90695	0.90787	—0.00092
79.578	20.422	82.643	17.357	0.90310	0.90399	—0 00087
100.000	0.000	100.000	0.000		0.86288	

TABLE XII.

Specific Gravities of Mixtures of Toluene I. and Carbon Bisulphide.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	CS_2.	C_7H_8.	CS_2.			
0.000	100.000	0.000	100.000		1.25958	
7.269	92.731	6.082	93.918	1.21888	1.21783	+0.00105
37.992	62.008	33.605	66.395	1.07229	1.06759	+0.00470
63.242	36.758	58.699	41.301	0.97587	0.97217	+0.00370
100.000	0.000	100.000	0.000		0.86288	

Table XIII.

Specific Gravities of Mixtures of Toluene II. and Acetic Ether II.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_4H_8O_2$.	C_7H_8.	$C_4H_8O_2$.			
0.000	100.000	0.000	100.000		0.89156	
15.708	84.292	15.129	84.871	0.88592	0.88588	+0.00006
45.301	54.699	44.202	55.798	0.87546	0.87529	+0.00017
71.255	28.745	70.335	29.665	0.86652	0.86636	+0.00016
100.000	0.000	100.000	0.000		0.85680	

Table XIV.

Specific Gravities of Mixtures of Acetic Ether II. and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_8O_2$.	CS_2.	$C_4H_8O_2$.	CS_2.			
0.000	100.000	0.000	100.000		1.25958	
16.359	83.641	14.451	85.549	1.17990	1.16956	+0.01034
39.246	60.754	35.811	64.189	1.08498	1.06877	+0.01621
66.413	33.587	63.069	36.931	0.98856	0.97681	+0.01175
100.000	0.000	100.000	0.000		0.89156	

Table XV.

Specific Gravities of Mixtures of Acetic Ether II. and Ethyl Iodide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_8O_2$.	C_2H_5I.	$C_4H_8O_2$.	C_2H_5I.			
0.000	100.000	0.000	100.000		1.93015	
21.799	78.201	33.073	66.927	1.53925	1.52760	+0.01265
64.427	32.573	78.585	21.415	1.08104	1.07553	+0.00551
100.000	0.000	100.000	0.000		0.89156	

Table XVI.

Specific Gravities of Mixtures of Ethyl Ether and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_{10}O$.	CS_2.	$C_4H_{10}O$.	CS_2.			
0.000	100.000	0.000	100.000		1.25959	
13.100	86.900	13.407	86.593	1.14342	1.14280	+0.00062
34.367	65.633	34.969	65.031	0.99455	0.99380	+0.00075
62.759	37.241	63.380	36.620	0.84725	0.84689	+0.00036
100.000	0.000	100.000	0.000		0.76942	

TABLE XVII.

Specific Gravities of Mixtures of Carbon Tetrachloride and Carbon Bisulphide.

Temperature, 20°.0. (Brown.)

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
CCl_4.	CS_2.	CCl_4.	CS_2.			
		0.000	100.000		1.26583	
		9.840	90.160	1.31527	1.31269	+0.00258
		19.474	80.526	1.35857	1.35430	+0.00427
		29.676	70.324	1.39976	1.39430	+0.00546
		39.974	60.026	1.43718	1.43102	+0.00616
		49.976	50.024	1.47009	1.46410	+0.00599
		59.161	40.839	1.49773	1.49216	+0.00457
		69.779	30.221	1.52698	1.52232	+0.00466
		80.231	19.769	1.55331	1.55005	+0.00326
		88.471	11.529	1.57253	1.57057	+0.00196
		100.000	0.000		1.59742	

Temperature, 25°.0. (Linebarger.)

0.000	100.000	0.000	100.000		1.25958	
28.271	71.729	16.285	83.715	1.33803	1.33397	+0.00406
57.150	42.850	39.942	60.058	1.42857	1.42298	+0.00559
85.772	14.228	74.844	25.156	1.53178	1.52729	+0.00449
100.000	0.000	100.000	0.000		1.58828	

TABLE XVIII.[1]

Specific Gravities of Mixtures of Carbon Bisulphide and Acetic Ether.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_8O_2$.	CS_2.	$C_4H_8O_2$.	CS_2.			
0.000	100.000	0.000	100.000		1.25958	
16.359	83.641	14.451	85.549	1.17990	1.16956	+0.01034
39.246	60.754	35.811	64.189	1.08498	1.06877	+0.01621
66.413	33.587	63.069	36.931	0.98856	0.97681	+0.01175
100.000	0.000	100.000	0.000		0.89156	

[1] The mixture containing 16.359 per cent. of acetic ether separated out into layers when cooled a little below 25.0.°

TABLE XIX.

Specific Gravities of Mixtures of Chloroform and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$CHCl_3$.	CS_2.	$CHCl_3$.	CS_2.			
0.900	100.000	0.000	100.000		1.25958	
28.696	71.304	20.940	79.060	1.31598	1.30877	+0.00721
62.557	34.443	51.518	48.482	1.38938	1.37919	+0.01019
79.361	20.639	70.976	29.024	1.42895	1.42130	+0.00765
93.909	6.091	90.749	9.251	1.46503	1.46197	+0.00316
100.000	0.000	100.000	0.000		1.48069	

TABLE XX.

Specific Gravities of Mixtures of Carbon Tetrachloride and Chloroform.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
CCl_4.	$CHCl_3$.	CCl_4.	$CHCl_3$.			
0.000	100.000	0.000	100.000		1.48069	
19.269	80.731	15.663	84.337	1.50018	1.49872	+0.00146
53.446	46.554	47.118	52.882	1.53820	1.53344	+0.00476
57.277	42.723	50.989	49.011	1.56805	1.56489	+0.00316
100.000	0.000	100.000	0.000		1.58828	

TABLE XXI.

Specific Gravities of Mixtures of Nitrobenzene and Acetic Ether I.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences
$C_6H_5NO_2$.	$C_4H_8O_2$.	$C_6H_5NO_2$.	$C_4H_8O_2$.			
0.000	100.000	0.000	100.000		0.89663	
22.896	77.104	17.530	82.470	0.95202	0.95669	—0.00467
56.100	43.900	47.770	52.230	1.04568	1.05318	—0.00760
75.530	24.470	68.870	31.130	1.10911	1.11618	—0.00707
100.000	0.000	100.000	0.000		1.20200	

TABLE XXII.

Specific Gravities of Mixtures of Toluene and Carbon Tetrachloride.

Temperature, 20.°o. (Brown.)

Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	CCl_4.			
0.000	100.000		1.59712	
20.706	79.294	1.43408	1.43447	—0.00039
40.594	59.406	1.28277	1.28442	—0.00165
47.661	52.339	1.23156	1.23202	—0.00047
50.540	49.460	1.21055	1.21090	—0.00035
60.166	39.834	1.14113	1.14130	—0.00017
70.231	29.769	1.06988	1.07013	—0.00025
79.920	20.080	1.00256	1.00265	—0.00009
100.000	0.000		0.86684	

TABLE XXIII.

Specific Gravities of Mixtures of Dichlorethane and Benzene.

Temperature, 20°.o. (Brown.)

Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_2H_4Cl_2$.			
0.000	100.000		1.25105	
20.477	79.523	1.16809	1.16587	+0.00222
39.527	60.473	1.09440	1.09139	+0.00301
59.900	40.100	1.01906	1.01622	+0.00284
79.522	20.478	0.94968	0.94790	+0.00178
100.000	0.000		0.88036	

TABLE XXIV.

Specific Gravities of Mixtures of Benzene and Dibromethane I.

Temperature, 20.°o. (Brown.)

Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_2H_4Br_2$.			
0.000	100.000		2.17053	
27.001	72.999	1.81638	1.81277	+0.00361
49.185	50.815	1.52864	1.52467	+0.00397
58.287	41.713	1.41142	1.40776	+0.00366
67.289	32.711	1.29597	1.29269	+0.00328
82.199	17.801	1.10577	1.10384	+0.00193
100.000	0.000		0.88036	

Specific Gravities of Mixtures of Benzene and Dibromethane II.

0.000	100.000		2.17626	
39.378	60.622	1.65811	1.65460	+0.00351
66.084	33.916	1.31256	1.30942	+0.00314
100.000	0.000		0.88036	

VI.

Discussion of Results.

If any amount of a pure liquid be mixed with any other amount of it under identical conditions of temperature and pressure, the volume of the resulting mixture is equal to the sums of the volumes of the amounts mixed, and all physical properties of the unmixed liquids persist in the mixture. If, however, two liquids of different chemical composition—be the difference ever so slight, and be the similarity of the physical properties of the liquids ever so great—are mixed, the resulting mixture does not necessarily have a volume equal to the sum of the volumes of its own components, although, in certain instances, this may be the case; generally there will occur a contraction or expansion in volume. It is interesting to seek an explanation for this behavior.

The simplest case that can perhaps be considered is this: two liquids, *A* and *B*, have no appreciable specific action upon one another; the attractions between the like molecules is of the same order as those between the unlike. The molecular actions being thus supposed to be independent of the chemical nature of the liquids, these might be expected to behave similarly to gases, and, when mixed, not to undergo any change in volume, were it not for the fact that the analogy fails in a most essential particular. A distinguishing feature between gases and liquids is the possession by the latter of a definite surface, and the exhibition of the so-called capillary phenomena. The cause of this surface and the capillary phenomena is to be found in the internal pressure, due to the interaction of the molecules and acting normally to the surface. This pressure it is, which determines the density of a liquid at any temperature, and its amount as well as the density, decreases in most cases with rise of temperature. Since the internal pressure is due to the attrac-

tions of the molecules of a liquid, any circumstance tending to diminish this action, occasions a falling off in the amount of the internal pressure. Rise of temperature lessens molecular attraction, and, as just stated, the internal pressure also; a dilution of the liquid by another without specific action in like manner reduces the molecular attraction and the internal pressure correspondingly. If, then, to the liquid *A* a small proportion of the liquid *B* be added, the number of molecules of *A* in the unit of surface or volume becomes smaller, so that the molecular attraction and internal pressure also become smaller; a decrease in the density or an increase in volume is the effect measurable by the experimental means at our command. As more and more of the liquid *B* is added to the liquid *A*, the internal pressure and the density becomes less and less. Now, entirely similar effects are caused by the addition of *A* to *B*; hence the minimum of internal pressure and density should be reached when about equal quantities of both liquids are mixed. It is to be concluded then that the mixing of normal liquid decreases the specific gravity.

Similar conclusions are arrived at by the introduction and use of the conception of osmotic pressure. When a small proportion of *A* is mixed with *B*, the molecules of *A* are in a way freed from their internal pressure, and behave as if in the gaseous state; they accordingly exert osmotic pressure, which acts against the internal pressure, so that the latter becomes reduced in amount. As *A* in *B*, so does *B* in *A* exert an osmotic pressure, the maximum of which is attained when about equal numbers of molecules of each liquid are contained in the mixture. But as osmotic and internal pressure are in inverse proportion, it follows that the mixture with the maximum osmotic presure must have the minimum internal pressure.

It is doubtful if there exist two liquids which are without appreciable specific action upon each other. The above considerations, then, as applying to an ideal state of affairs, can lead only to approximate results. But an examination of the data given in the previous section shows that in the majority of cases the calculated density is greater than that found ex-

perimentally. The differences are generally small and have their maximum value when the mixture in question is made up of about equal proportions of its constituents; in no case do points of inflection occur. This is quite in accordance with the developments of the foregoing paragraphs.

Some mixtures there are, however, that do not behave in this normal way; in them a contraction of volume attends the mixing and their densities are found to be greater than those calculated. It may seem natural to attribute this behavior to some specific actions between the molecules of the liquids mixed. Still, certain mixtures, as that of toluene and monochlorbenzene, are made up of such chemically similar liquids, that it seems that recourse should not be had to assumptions of specific molecular attractions. In other mixtures, however, it seems quite allowable to make such assumptions. Thus, if benzene, toluene, or acetic ether be mixed with nitrobenzene, the density of the resulting mixture is greater than that calculated by the rule of mixtures, although any of the three first mentioned liquids when mixed with another of them shows the normal behavior, *viz.*, expansion. In this case, then, there seems to reside in the nitrobenzene a power of drawing the molecules of mixtures of which it is a component closer together.

In a mixture of benzene or toluene with carbon tetrachloride, the observed density is very slightly greater than the theoretical. Yet when the last-named liquid is mixed with chloroform, the observed densities are relatively considerably less than those calculated. It would appear that these liquids are so normal and so similar physically and chemically that in their mixtures the normal behavior would be found; it may be called to mind that these very liquids—chloroform and carbon tetrachloride—were found to behave somewhat irregularly in the vapor tensions of their mixtures[1] and in the heat phenomina attendant upon their mixing.[2] The remark of Brown[3] is applicable here, who, in discussing his results,

[1] See my paper "On the Vapor Tensions of Mixtures of Volatile Liquids." J. Am. Chem. Soc., **17**, 690, (1895).

[2] See my paper "On the Heat Effect of Mixing Liquids." The Physical Review, 1896.

[3] *Loc. cit.*

obtained with mixtures of benzene and toluene with carbon tetrachloride, writes: "The numbers form a remarkable confirmation of the supposition that these changes are dependent on the chemical character of the molecules, and entirely independent of such physical properties as vapor-tension, molecular volume, etc." It is indeed remarkable that the differences between the calculated and observed values of mixtures of carbon tetrachloride with either benzene or toluene are almost the same, as is clearly shown by the curves that Brown has published.[1]

It must be concluded that with our present meager data very few generalities can be drawn as to a connection between the chemical or physical properties of liquids and their changes of volume when mixed.

A point which it may be worth while to dwell upon is the amount of the differences between the observed and the calculated densities in connection with the possibility of a slight degree of molecular polymerization. When the mixtures are made up of liquids that are strictly normal, as the hydrocarbons, ethers, etc., the differences are found to be but slight, seldom exceeding more than a ten-thousandth of the density. When one of the compounds is somewhat associated, the differences are greater. Now, Ramsay and Aston[2] have found carbon bisulphide to be slightly associated at low temperatures, and we see, indeed, that in those mixtures which contain carbon bisulphide as a constituent, the differences of density—theoretical and observed—amount to several thousandths or even hundredths. We have here then, a criterion of molecular polymerization in liquids; when a liquid mixed with another which is recognized to be strictly normal, forms mixtures whose specific gravities differ considerably from those calculable by the rule of mixtures, that liquid is composed of more or less associated molecules.

With considerable differences between the values of calculated and observed specific gravities stands in close connection the phenomenon of layer formation. A glance at Table XVIII, p. 446, shows differences in the last column amounting to hundredths of the amount of the quantity measured,

[1] *Loc. cit.* [2] Ztschr. phys. Chem., **15**, 89, (1894).

and for certain proportions of the liquids layer formation is observed.

Contributions from the Chemical Laboratory of Cornell University.

DIANTHRANOL—A DIHYDROXYL DERIVATIVE OF DIANTHRACENE.

By W. R. Orndorff and C. L. Bliss.

In a recent article on dianthracene[1] by Orndorff and Cameron, it was stated that a solution of anthranol in benzene suffered a change in the direct sunlight, similar to that noticed in case of solutions of anthracene itself. To the product formed from anthranol under these conditions, the provisional name dianthranol was given on account of the resemblance in its mode of formation and general physical properties to dianthracene. Since the publication of the article above referred to, a considerable quantity of this substance has been made, and a thorough study of it has shown that the above supposition in regard to it being a dihydroxyl derivative of dianthracene is correct.

Anthranol, $C_6H_4\begin{cases}C(OH)\\|\\CH\end{cases}>C_6H_4$, was prepared and studied by Liebermann, first in connection with Topf[1] and then with Gimbel.[2] In both cases it was made by the reduction of anthraquinone, according to the equation,

$$C_{14}H_8O_2 + 2H_2 = C_{14}H_{10}O + H_2O.$$

After giving the details of their method of preparation of this substance and describing its properties, Liebermann and Topf state in regard to it that "Vielfaches Umkrystallisiren oder längeres Stehen ihrer Lösungen verträgt sie nicht; die dann erhaltenen Krystalle lösen sich bald nur noch zum geringen Theile in Alkali. In trockenem Zustand hält sie sich länger, selbst in Jahre alten Präparaten lässt sich oft neben veränderter Substanz unverändertes Anthranol nachweisen. Als Erkennungsmittel des Anthranols dient die gelbe Lösung desselben in Alkali.

Durch Kohlensäure wird aus dieser Lösung das Anthranol unter Entfärbung ausgefällt; schüttelt man die

[1] This Journal, **17**, 517. [2] Ann. Chem. (Liebig), **212**, 6.
[3] Ber. d. chem. Ges., **20**, 1854. (1887).

Lösung mit Luft so tritt ebenfalls nach einiger Zeit, wenn auch meist nicht ganz vollständige Entfärbung der Flüssigkeit unter Abscheidung eines weissen Niederschlags ein. Es war zu vermuthen, dass derselbe, sowie überhaupt die an der Luft veränderte Substanz, aus Anthrachinon bestehen würde. Letzteres liess sich auch immer leicht in dem Umwandlungsproduct nachweisen und durch Krystallisation abtrennen, doch geht die Oxydation durch ein Zwischenstadium hindurch, welches nicht in reiner Form erhalten wurde."

No other statement occurs in the literature concerning this change in solutions of anthranol, nor has the product formed ever been investigated. As it seemed quite likely that this change was connected with the action of light on solutions of anthranol observed by Orndorff and Cameron, and that the product formed was the same in both cases, the present investigation was undertaken to show whether this supposition was correct or not, and also to determine the relation of this product to anthranol itself.

Experimental.

The anthranol used in this work was made and purified according to the method given by Liebermann and Gimbel by the reduction of pure anthraquinone in acetic acid solution with tin and hydrochloric acid. It melted with decomposition at 163–170° C. (uncor.) and crystallized in lemon-yellow colored needles. A solution of this anthranol in benzene was exposed to the action of the bright sunlight for some weeks during the summer of 1895. The solution at first became colored dark green with a bluish fluorescence, then yellow, and finally, after a few days, reddish-yellow, some white crystals, entirely different in appearance from crystals of anthranol, separating out. These crystals were filtered off, and a second crop having a yellow color was obtained from the filtrate after some of the solvent had been distilled off. In the mother-liquor there remained a small amount of unchanged anthranol and some anthraquinone. The crystals were then purified by recrystallizing several times from benzene, using bone-black to remove the yellow color. It was found exceedingly difficult to get rid of this yellow coloring material, and,

though the benzene solution was treated with bone-black a number of times, the crystals finally obtained still had a marked yellow tinge. They melted at 245–255° C. and sometimes as high as 260–263° (depending on the rapidity with which they were heated), and always with decomposition. An analysis of the best product melting at 260–263° C. gave the following results:

I. 0.1584 gram gave 0.0650 gram H_2O and 0.5043 gram CO_2.
II. 0.1325 " " 0.0560 " " " 0.4219 " "

	Found. I.	Found. II.	Calculated for $(C_{14}H_{10}O)_x$.
Carbon	86.83	86.84	86.60
Hydrogen	4.56	4.69	5.15
Oxygen (by difference)	8.61	8.47	8.25

These results show that the substance formed by the action of light on anthranol has the same percentage composition as the anthranol itself. As it seemed probable that the new substance was white when pure, we endeavored to purify our product further. It was almost insoluble in ether and so slightly soluble in alcohol that these solvents could not be used for recrystallizing. In chloroform, on the other hand, it was so very soluble that this solvent was also excluded. When boiled with acetone the yellow material appeared to go into solution more readily and separated out first on cooling, so that by careful management an almost white product was obtained, and by repeating the process pure white crystals resulted. These crystals, which melted at 255–260° C. (uncor.) with decomposition were then analyzed with the following results:

0.2180 gram gave 0.0891 gram H_2O and 0.6956 gram CO_2.

	Found.	Calculated for $(C_{14}H_{10}O)_x$.
Carbon	87.02	86.60
Hydrogen	4.54	5.15
Oxygen (by difference)	8.44	8.25

Some preliminary experiments having shown that the melting-point of anthranol crystallized from high-boiling solvents was raised very markedly, and that the product formed appeared to be identical with that resulting from the action of light on solutions of anthranol, we next endeavored to make

the new product by boiling a solution of pure anthranol in xylene for a long time. After heating the solution in a flask connected with an inverted condenser for twelve hours, the change appeared to be complete. On cooling, crystals resembling those obtained by the action of light on solutions of anthranol separated out, and, on concentrating the filtrate from these, a second crop of crystals was obtained. This crude product, melting at 240–250° C. (uncor.), was purified by fractional crystallization from glacial acetic acid and then from benzene, using bone-black to remove the yellow color of the solutions. The crystals made in this way were pure white, and melted with decomposition at 246–251° C. (uncor.), using a standardized thermometer. An analysis gave the following results:

I. 0.1703 gram gave 0.0748 gram H_2O and 0.5434 gram CO_2.
II. 0.2009 " " 0.0858 " " " 0.6402 " "

	Found. I.	Found. II.	Calculated for $(C_{14}H_{10}O)_x$.
Carbon	87.01	86.91	86.60
Hydrogen	4.88	4.74	5.15
Oxygen (by difference)	8.11	8.35	8.25

These results show that the product formed on boiling a solution of anthranol in xylene is the same as that obtained by the action of light on a solution of anthranol in benzene, and that the product has the same percentage composition as anthranol itself.

We next investigated the product formed when a solution of anthranol in potassium hydroxide is shaken with air. This substance is regarded by Liebermann as an intermediate product between anthranol and anthraquinone, though he gives no analyses and probably did not have the substance in a pure form. Pure anthranol was dissolved in a hot dilute solution of potassium hydroxide, the solution filtered and a current of air, freed from carbon dioxide, passed through the reddish yellow-colored solution until it was almost decolorized. A white precipitate was formed, which appeared to be totally insoluble in the solution of potassium hydroxide. This was decanted off, washed with a fresh solution of potassium hydroxide, then with hot water,

filtered, dried, and recrystallized from acetone. The crystals were yellow-colored at first, but by boiling the solution with bone-black, or by decolorizing it with sulphur dioxide, we finally obtained them in beautiful transparent tablets, melting at 250° C., and showing all the characteristic of the dianthranol prepared by other methods.

From these results it will be seen that the product formed by the oxidation of anthranol in caustic potash solution is the same as that obtained by the action of light on solutions of this substance, as well as by heating a solution of anthranol in xylene. In order to determine the exact relation between anthranol and this new product, both having the same percentage composition, molecular weight estimations were now made by the boiling-point method, using the apparatus[1] recently described by Orndorff and Cameron for this purpose. The following are the results obtained with the new product:

DIANTHRANOL.

$C_{14}H_{10}O = 194$; $C_{28}H_{10}O_2 = 388$.

Solvent: *Chloroform*.

Boiling-point 60°.2 C. at 741.7 mm. barometric pressure.

Molecular elevation for 100 grams 36.6°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	201.23	0.6527	0.3244	0.028°	739.2	424
2	"	1.1834	0.5881	0.049	739.1	439
3	"	1.6134	0.8018	0.069	739.0	425
4	"	1.9671	0.9775	0.086	738.9	416

Barometer 739.3–738.9 mm.

Molecular weight at infinite dilution, **405**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
5	213.90	1.0562	0.4938	0.041°	739.3	441
6	"	2.0545	0.9605	0.084	739.6	418

Solvent: *Benzene*.

Boiling-point 79.6° C. at 744.5 mm. barometric pressure.

Molecular elevation for 100 grams 26.6°.

[1] This JOURNAL, **17**, 517.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
7	113.03	0.7972	0.7053	0.050°	743.5	375
8	"	1.4789	1.3084	0.094	743.6	370

These results show that the formula of the new compound is $C_{28}H_{20}O_2$, but, as the molecular weight of anthranol itself is not known, it is impossible to say whether this product is an isomer or a polymer of anthranol. We therefore next determined the molecular weight of anthranol, using the same method and apparatus as before, and working with the purest material we could prepare. The results follow :

ANTHRANOL.

$C_{14}H_{10}O = 194$; $C_{28}H_{20}O_2 = 388$.

Solvent: *Benzene.*

Boiling-point 79.6° C. at 744.5 mm. barometric pressure.

Molecular elevation for 100 grams 26.6°.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	119.88	0.5742	0.4790	0.064°	743.7	199
2	"	0.9343	0.7794	0.095	"	218
3	"	1.2782	1.0663	0.129	"	220
4	"	1.5100	1.2596	0.150	"	223

Barometer 743.6–743.7 mm.

Molecular weight at infinite dilution 186

We see from these results that the new substance has double the molecular weight of anthranol, and that the relations between it and anthranol is exactly the same as that existing between dianthracene and anthracene. The name dianthranol serves very well to recall this relation, and also to show that it is a derivative of dianthracene.

The dianthranol made by one of the above processes and crystallized first from glacial acetic acid and then from benzene, is a beautiful product crystallizing in colorless tabular or columnar crystals. The pure substance melted with decomposition at about 250° C., sometimes as low as 246° C. and even as high as 255° C., depending on the rapidity with which the material was heated. It is almost insoluble in ether, slightly soluble in alcohol, more soluble in acetone, glacial acetic acid and benzene, and

very soluble in chloroform. In solutions of the alkalies dianthranol is insoluble even on long boiling. This serves as an excellent method to separate dianthranol from anthranol. When a solution of dianthranol in benzene is allowed to evaporate slowly to dryness in contact with the air, it is partially oxidized to anthraquinone.

Some dianthranol was heated in a test-tube in a sulphuric-acid bath to its melting-point, and kept at this temperature for about an hour. The material in the tube blackened and seemed to be entirely decomposed. After cooling, however, some yellow needles were found to have sublimed out of the black product. These were completely soluble in a boiling solution of potassium hydroxide with a yellow color, and were again precipitated on the addition of hydrochloric acid. They melted at 160°–180° C. with decomposition, and gave none of the tests for anthraquinone. The substance appeared to be anthranol, but the quantity formed was too small for analysis. It seems, therefore, quite probable that dianthranol undergoes at its melting-point a change into anthranol, similar to that observed when dianthracene is heated to its melting-point, and is converted into anthracene. As anthranol melts with decomposition at 163–170° C., it is not at all surprising that this change is far from quantitative. Anthranol crystallizes in the orthorhombic system, while dianthranol is monoclinic, as will be seen from the following crystallographic measurements, kindly made for us by Professor A. C. Gill, of the Mineralogical Department of this University. The anthranol and dianthranol measured were both recrystallized from benzene.

Anthranol.

"The crystals of anthranol are long six-sided needles of a pale straw-yellow color. Those measured were from 5 to 20 mm. in length, and scarcely $\frac{1}{2}$ mm. in diameter. The parallel extinction, taken together with the fact that four of the six faces are equally inclined to the remaining two, establishes the orthorhombic form of these acicular crystals. No reflecting terminal planes could be found, hence the length of the vertical axis was only approximately determined by measuring the

plane angle of the end faces on the brachypinacoid. The average of 11 measurements ranging from 124°40′ to 131° was 127°20′, hence :

$$a : b : c = 0.8124 : 1 : 0.402\ (?)$$

Faces measured with goniometer ; ∞P (110) and $\infty P\bar{\infty}$ (100). $110 : 1\bar{1}0 = 78°11'$; $110 : 010 = 50°56'$ (calculated from other angle, 50°54′30″).

"Anthranol has an *extremely* high double refraction and dispersion.

"The crystals show a good basal cleavage."

Dianthranol.

" The crystals of dianthranol are monoclinic, usually elongated in the direction of the ortho-axis, and often tabular parallel to the orthodome ($\bar{1}01$).

The results of the measurements of eighteen crystals are as follows : $\dot{a} : \dot{b} : \dot{c} = 2.307 : 1 : 1.7701$; $\beta = 87°3'30''$.

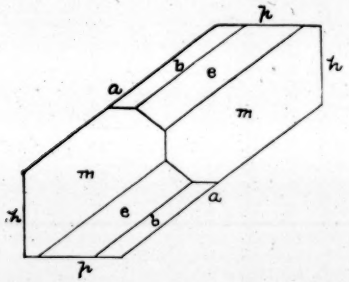
The forms observed, $a = +P\bar{\infty}$ ($\bar{1}01$) ; $p = oP$ (001) ; $h = \infty P\bar{\infty}$ (100) ; $m = \infty P$ (110) ; $e = P_{\dot{\infty}}$ (011) ; and $b = +\frac{1}{2}P(\bar{2}21)$.

A list of the principal angles follows :

	Measured.	No. of measurements.	Calculated.
110 : 100	66°33′30″	32	
100 : 001	89°3′30″	25	
100 : 10$\bar{1}$	53°4′40″	26	
110 : $\bar{1}$10	46°52′40″	14	46°53′
001 : $\bar{1}$01	37°52′11″	24	37°51′50″
001 : 011	60°28′	2	60°32′42″
$\bar{1}$10 : $\bar{1}$01	76°10′10″	16	76°10′26″
001 : $\bar{1}$10	90°23′	2	90°22′28″
011 : $\bar{1}$00	90°34′	1	90°27′44″
$\bar{1}$01 : $\bar{2}$21	42°33′30″	4	42°34′9″
001 : $\bar{2}$21	44°5′	2	44°9′33″

"The accompanying figure shows the projection of the observed faces on the clinopinacoid. There is great variation in the relative development of the end-faces, though the b-faces are usually much smaller than here shown."

"The plane of the optical axes is the clinopinacoid (010), and the inclined dispersion is plainly seen in thin crystals. One optical axis is nearly normal to the orthodome ($\bar{1}01$), which is usually the most extensive face on the crystals. More rarely, however, the base (001) is largely developed,



and in such crystals the acute bisectrix may be seen to lie in the acute angle β, somewhat inclined from a position perpendicular to the base."

The change of anthranol into dianthranol seems to be generally accompanied by a partial oxidation of some of the anthranol to anthraquinone, as the latter substance can always be detected, (sometimes only in very small quantity) in the crude dianthranol. That heat alone will not cause the change was shown by boiling some of the anthranol in solution in xylene in an atmosphere of dry carbon dioxide. No change was noticed in the melting-point of the crystals obtained from this solution after boiling for an hour and a half, and even after eight hours boiling very little change had occurred, though the melting-point had now risen from 162–170° C. to 172–185° C. A solution in mesitylene, after being boiled for

four hours in the same way, desposited on cooling crystals, which appeared for the most part to be anthranol, though they began to melt at 180°, and were not completely fused till the temperature reached 265° C. These crystals gave a slight reaction also for anthraquinone.[1] Even where the change is brought about by the action of sunlight on solutions of anthranol in benzene, anthraquinone was found in the mother-liquors from which the dianthranol crystallized out. When the dianthranol was made by passing a current of air through an alkaline solution of anthranol, anthraquinone was detected in the crude product, as Lieberman also found, though it may have resulted here from the further oxidation of some of the dianthranol.

We next endeavored to determine if the hydroxyl groups underwent any change when anthranol is converted into dianthranol. This appeared probable at first from the fact that the dianthranol was insoluble in solutions of the caustic alkalies even on long continued boiling. To solve this question we tried to make the diacetyl derivative of dianthranol. It was found exceedingly difficult to replace the hydrogen atoms by acetyl groups, but by heating the substance in a sealed tube to 180–190° C. with a considerable excess of acetic anhydride and some fused sodium acetate we finally succeeded. The crystals formed in the sealed tubes, which were of a dark red color, were filtered from the liquid, washed with water, dissolved in hot alcohol, and this solution boiled with bone-black to remove the color. Water was then added to the hot alcoholic solution. On cooling, reddish-yellow leaflets crystallized out. After repeating this process of purification several times a pure product was obtained, consisting of light yellow-colored plates, which melted with decomposition at 276–279°C. An analysis of this product gave the following results, which show that the substance is a diacetyl derivative of dianthranol:

0.0740 gram gave 0.0358 gram H_2O and 0.2210 gram CO_2.

[1] Anthraquinone was detected here by boiling a small amount of the substance with zinc dust and dilute caustic soda solution, when a red color appeared. Pure anthranol and dianthranol will not give this reaction.

	Found.	Calculated for $\left(C_6H_4<\begin{matrix}CH.\\CO(C_2H_3O)\end{matrix}>C_6H_4.\right)_2$
Carbon	81.45	81.35
Hydrogen	5.37	5.09
Oxygen (by difference)	13.18	13.56

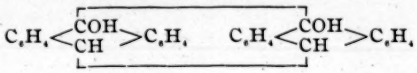
This diacetyldianthranol was very soluble in chloroform, the solution having a beautiful bluish-violet fluorescence. As this fluorescence was not permanent, however, but gradually disappeared on standing, it is probably due to some impurity. Diacetyldianthranol is difficultly soluble in benzene and alcohol, and differs very markedly in other respects from the acetyl derivative of anthranol which has the same percentage composition. Its melting-point, crystal form, and general physical properties are different, so that there seems to be do doubt that the substance is diacetyldianthranol. Attempts to determine the presence of the acetyl groups qualitatively by heating the substance with alcohol and sulphuric acid gave unsatisfactory results, as the product seemed not to be acted on by these reagents.

Theoretical.

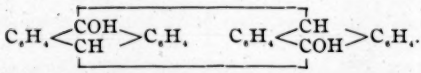
The formula of anthranol is undoubtedly $C_{14}H_{10}O$, as has been proved by the analysis and our determination of its molecular weight. The structural formula has been shown by Liebermann and Topf to be $C_6H_4\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}COH\\|\\CH\end{matrix}\begin{matrix}\diagup\\\diagdown\end{matrix}C_6H_4$, and not $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>C_6H_4$ from the fact that it forms an acetyl derivative $C_6H_4\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}C\ O.C_2H_3O\\|\\CH\end{matrix}\begin{matrix}\diagup\\\diagdown\end{matrix}C_6H_4$.

The formula of dianthranol has been shown to be $C_{28}H_{20}O_2$, and it has been proved by the formation of the diacetyl derivative that it contains two hydroxyl groups. It appears, therefore, to be made up of two molecules of anthranol joined in such a way as to leave the two hydroxyl groups intact. This may be conceived as taking place by the breaking of the para bond between the two γ-carbon atoms, and the joining of

the two anthranol groups thus formed. This may take place in two ways, as shown by the following formulas:



and



Both formulas would represent the dianthranol as a γ-dihydroxyl derivative of dianthracene. The second of these formulas, however, would seem the more probable for dianthranol, for the reason that here like groups are represented as far away from each other as possible, while the unlike groups —CH and —COH are joined together. The crystallographic study of this substance also leads to the same conclusion. Dianthranol is undoubtedly monoclinic, as shown by Dr. Gill's measurements, and it will be seen by a careful study of the stereochemical model of the second formula that it also has a monoclinic symmetry while that of the first formula has an orthorhombic symmetry. The molecule of dianthranol is so large that it is very probable that the symmetry of the crystal is here determined by the symmetry of the molecule. Again it will be noticed from Dr. Gill's report that, while dianthranol is certainly monoclinic, it approaches very closely to the orthorhombic system, the angle β being 87°3′30″, which is very nearly 90°. This agrees with the second formula, which possesses a monoclinic symmetry, to be sure, but which is very nearly, though not quite, orthorhombic. The fact that dianthranol has none of the properties characteristic of a pinacone, which it would probably show if it were constituted as the first formula represents it, is also in favor of the second formula for this substance. The insolubility of the compound in potassium hydroxide solution is easily understood, when we consider that it is a tertiary alcohol and not a phenol.

Anthranol itself is not soluble in alkaline solution in the cold, but only on boiling. Liebermann suggests that

this solubility of anthranol may be due to the formation of an addition-product like $C_6H_4<\begin{matrix}CHOK\\CHOH\end{matrix}>C_6H_4$. In the case of dianthranol, the formation of such an addition-product is not possible.

The formation of dianthracene from anthracene by the action of the sunlight was shown to be probably due to the breaking of the para bond between the γ-carbon atoms and the union of the two molecules of anthracene to one of dianthracene. The transformation of anthranol to dianthranol is probably due to the same cause. Here, however, it is worthy of note that this change may be brought about by oxidation as well as by the action of light.

CORNELL UNIVERSITY, ITHACA, N. Y.,
March, 1896.

Contribution from the Chemical Laboratory of Harvard College.

XCIV.—BROMINE DERIVATIVES OF METAPHENYLENE DIAMINE.[1]

BY C. LORING JACKSON AND SIDNEY CALVERT.

INTRODUCTION.

In the course of an extended investigation of the behavior of the tribromdinitrobenzol, melting at 192°, carried on now for some years in this laboratory, we took up the reduction of this substance with tin and hydrochloric acid, since, if the bromine was not removed, new bromine derivatives of metaphenylene diamine must be obtained, or, on the other hand, the replacement of the bromine by hydrogen would be of interest, because cases in which a halogen is removed from the benzol ring under these conditions, are far from common. As, however, two of those already observed had occurred in the work on derivatives of tribromdinitrobenzol done in this laboratory, we had reason to hope that the proposed experiments might furnish us with an additional case, and contribute something toward determining the conditions under which this replacement of bromine by hydrogen takes place. After we had begun our work there appeared a paper[2] by

[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Ber. d. chem. Ges., **28**, 552.

Schlieper on the removal of bromine from aromatic compounds by tin and hydrochloric acid, in which he announced his intention of making an extended research in this field; we accordingly wrote to Victor Meyer, under whose direction Schlieper was working, asking if we might finish our work, and he has with great courtesy given us permission to do so.

We have succeeded in finding only the following cases in which bromine is replaced by hydrogen in aromatic compounds by reduction with tin and hydrochloric acid. Unsymmetrical brommetadinitrobenzol gives metaphenylene diamine.[1] Tribromdinitrobenzol sulphonic acid gives bromdiamidobenzolsulphonic acid.[2] Dibromdinitrophenylmalonic ester gives bromamidoxindol,[3] nitrite of bromdinitrophenylmalonic ester gives amidoxyoxindol.[4] Bromnitrophenol gives amidophenol, and bromnitranisol gives amidoanisol.[5] Metabromorthonitrobenzoic acid and its isomeric form both give anthranilic acid[6] and Hübner also states[7] that he obtained small quantities of orthophenylene diamine from nitroparabromaniline, but that the principal product was the bromphenylene diamine; this, however, seems to be the only case observed, and none are recorded to our knowledge in the para series. We could find no record of the removal of other halogens under these conditions, until Schlieper published a second paper[8] (after our work on tribromdinitrobenzol was finished), in which he describes the reduction of chlor- and iodnitrophenols or anisols, when he found that iodine was removed just as bromine was, but that chlorine was not replaced by hydrogen. On the other hand he found that bromine could not be removed from derivatives of ortho- or paranitrophenols, as was to be expected from the work of previous observers. From his experiments he infers that bromine or iodine is replaced by hydrogen under the influence of tin and hydrochloric acid, when it stands in the ortho position to the two negative groups (OH. Br. NO_2. 1, 2, 3), although he has not yet succeeded

[1] Zincke and Sintenis: Ber. d. chem. Ges., **5**, 792.
[2] Baessmann: Ann. Chem. (Liebig), **191**, 244.
[3] Jackson and Bancroft: This JOURNAL **12**, 301.
[4] Jackson and Bentley: This JOURNAL **14**, 360.
[5] Schlieper: Ber. d. chem. Ges., **25**, 552.
[6] Hübner and Petermann: Ann. Chem. (Liebig), **149**. 135.
[7] Ann. Chem. (Liebig), **209**, 360. [8] Ber. d. chem. Ges., **26**, 2465.

in bringing an absolute proof that this is the constitution of the substances with which he worked.

Our experiments proved that when tribromdinitrobenzol was treated with a mixture of tin, hydrochloric acid, and a little alcohol,[1] all three of the atoms of bromine were replaced by hydrogen, the product being metaphenylene diamine. Schlieper's inference given in the preceding paragraph, therefore, is not of general application, as, if this were the case, only one atom of bromine would have been removed from the tribromdinitrobenzol, since only one of them is in the ortho position to both of the nitro groups, the constitution of this substance being Br. NO_2. Br. NO_2. Br. H. It is to be observed also that the conversion of unsymmetrical brommetadinitrobenzol into metaphenylene diamine, observed by Zincke and Sintenis, is not in harmony with this inference of Schlieper. Although, therefore, the diortho position is not essential to the removal of bromine by tin and hydrochloric acid, there is no doubt that Schlieper is right in considering it the most favorable position for this purpose, as the replacement by hydrogen of an atom of bromine standing between two nitro groups has been repeatedly observed in this laboratory with comparatively weak reducing agents, such as sodium malonic ester, and probably sodium acetacetic ester, or sodic ethylate.

In trying to find the cause of the replacement of all three atoms of bromine by hydrogen in the reduction of tribromdinitrobenzol, the most obvious theory was that the attachment of the atoms of bromine to the benzol ring was weakened by the presence of the two negative nitro groups, as is so frequently observed in other reactions. If this was the case, the bromine would be removed before the nitro groups were reduced, and tribromphenylene diamine would not lose its bromine on treatment with tin and hydrochloric acid. Upon trying this experiment, however, we found that the whole of the bromine was removed from the tribromdiamine as easily as from tribromdinitrobenzol.[2] It follows, therefore, that the nitro groups

[1] Schlieper used stannous chloride and hydrochloric acid in his work, and it is possible that this difference may have modified the result.

[2] Other reagents, for instance sodic ethylate or sodic hydrate, do not remove bromine from the diamine.

are not the cause of the easy removal of the three atoms of bromine in the reduction of tribromdinitrobenzol. A parallel experiment with dibromphenylene diamine showed that this substance gave up its bromine with much more difficulty than the corresponding tribrom compound, for, whereas the tribrom derivative was converted into phenylene diamine in a few minutes, it took over twelve hours to bring about the same change in the dibrom compound. It is evident from these unexpected results that the removal of the bromine atoms depends in part upon their position toward each other, and this is not strange, as in other cases it has been observed that three bromine atoms, when in the symmetrical position in a benzol ring, are more loosely attached than two in the meta position ; but this is not the only cause of their removal, since symmetrical tribrombenzol is not reduced by tin and hydrochloric acid. It would seem, therefore, that the replacement of these atoms of bromine is caused principally by the fact that there are other radicals attached to the ring, with little regard to the nature of these radicals, as the highly positive amido groups apparently produce the same effect as the highly negative nitro radicals. An additional argument for this conclusion was furnished by experiments on the reduction of tribromaniline which was converted into dibromaniline by the action of tin and hydrochloric acid for a few hours. From the facts at present known we are unable to deduce any rule in regard to the positions which these other radicals must occupy in order to cause the replacement of bromine by hydrogen, when the compound is treated with tin and hydrochloric acid.

After we had found, as just described, that the bromine was removed by the action of tin and hydrochloric acid upon tribromdinitrobenzol, we turned our attention to the study of the bromine derivatives of metaphenylene diamine, as only one of these had been described,— a dibromphenylene diamine, which Hollemann[1] stated he had obtained by the action of bromine water on the chloride of phenylene diamine. He gives, however, neither melting-point nor analysis of his substance. Upon trying to repeat his preparation we found that bromine

[1] Ztschr. Chem. 1865, 555.

water converted the chloride of phenylene diamine (or the free base suspended in water) into a tribromphenylene diamine melting at 158°. As the product is the same, when an insufficient quantity of bromine is used, a portion of the phenylene diamine remaining unaltered in this case, the statement of Hollemann must have rested on an error of observation. A paper by Vaubel,[1] which appeared after our work on this subject was finished, confirms our result, as he found by a volumetric method that three atoms of bromine are substituted for hydrogen in the molecule of phenylene diamine, when it is treated with a mixture of potassic bromide, sulphuric acid, and potassic bromate. We have made the same tibromphenylene diamine by the action of zinc dust and acetic acid on the tribromdinitrobenzol; this method of preparation proves that its constitution is Br. NH_2. Br. NH_2. Br. H.

A dibromphenylene diamine can be obtained by the action of bromine in excess upon phenylene diacetamide. The dibromphenylene diacetamide melts at 259° to 260°; the free base at 135°. We have not succeeded in determining the constitution of this dibromphenylene diamine. Nor have we obtained the corresponding monobromphenylene diamine. A monobromphenylene diamine belonging to another series was obtained, however, by reducing tetrabromdinitrobenzol (melting-point 227°) with tin and hydrochloric acid, it melts at 93°–94°, and from our experiments on the reduction of tribromdinitrobenzol there can be little doubt that it has the symmetrical constitution Br. H. NH_2. H. NH_2. H. When treated with bromine three atoms are substituted for three of hydrogen in its molecule, and the tetrabromphenylene diamine is formed, which melts at 212°–213°.

The presence of the bromine in the molecule of metaphenylene diamine has a strong effect on its tendency to form salts and on the composition of the salts formed. The tetrabrom and tribrom compounds do not form salts under ordinary conditions, but tribromphenylene diamine can be converted into its chloride by passing hydrochloric acid through a solution of it in benzol; this salt, however, gives up part of its hydrochloric acid at ordinary temperatures, the whole of it at

[1] J. prakt. Chem. [2], **48**, 75.

100°. The dibromphenylene diamine, on the other hand, forms salts more easily, and its chloride is only partially decomposed at 100°, while the bromide of this base seems to be even more stable. All three of these salts contain but one molecule of the acid, the chloride of dibromphenylene diamine, for example, having the following formula $C_6H_2Br_2NH_2ClNH_2$. The monobromphenylene diamine forms salts still more easily, and they are also more stable. The bromide contains two molecules of hydrobromic acid, having the formula $C_6H_3Br(NH_2Br)_2$. We have also prepared the tribromphenylene diacetamide, which does not melt at 330°, and the tribromphenylene diurethane melting at 212°.

Experimental Part.

Tribrommetaphenylene Diamine, $C_6HBr_3(NH_2)_2$.

The most convenient method for preparing this substance consists in passing a stream of air and bromine vapor into a solution containing metaphenylene diamine, for instance, that obtained by adding sodic hydrate or carbonate to the product of the reduction of metadinitrobenzol with tin and hydrochloric acid until all the tin is precipitated and filtering out the hydrate of tin. In adding the bromine an excess must be avoided, as this turns the product black, and we have therefore found it well to filter the precipitate out by means of cheese-cloth as fast as a sufficient quantity of it was formed, continuing the action of the bromine vapor on the successive filtrates as long as a precipitate appeared. The crude product, which was always dark colored, was dried, and then crystallized from alcohol containing a little benzol until it showed the constant melting-point 158°, when it was dried at 100° and analyzed with the following results:—

I. 0.1459 gram of the substance gave by the method of Carius 0.2392 gram of argentic bromide.

II. 0.2022 gram of the substance gave 14.65 cc. of nitrogen at a temperature of 19° and a pressure of 771.9 mm.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found. I.	II.
Bromine	69.56	69.78	...
Nitrogen	8.11	....	8.21

These analyses prove that the substance is tribromphenylene diamine, and therefore our experimental result does not agree with that of Hollemann,[1] who stated that he obtained a dibromphenylene diamine by the action of bromine water on a solution of the chloride of phenylene diamine. As it was possible that this difference in the results of the action might be due to the fact that Hollemann used a salt of phenylene diamine, whereas we used in our first experiments the free base dissolved and suspended in water, we repeated our experiment with a solution of the chloride of phenylene diamine, and obtained precisely the same result as with the free base, that is, the tribromphenylene diamine melting at 158°. We are therefore forced to the conclusion that Hollemann's statement is due to an error in observation.

Properties.—Tribromphenylene diamine crystallized from alcohol appears in long slender needles united longitudinally into ribbons with the ends serrated so strongly that they look like combs. It is white, with marked silky lustre, and melts at 158°. It is not very soluble in cold but freely in hot alcohol; somewhat more soluble in methyl than ethyl alcohol; freely soluble in ether, benzol, chloroform, glacial acetic acid, or carbonic disulphide; very slightly soluble in ligroïn, but good crystals may be obtained from its solution in hot ligroïn; essentially insoluble in water. Strong hydrochloric acid dissolves it easily in the cold, depositing after long standing white transparent crystals which soon turn brown; on heating the solution in hydrochloric acid it turned dark brown, almost black, showing decomposition of the substance; the formation of a similar nearly black decomposition-product was brought about at once by cold strong nitric acid. Cold strong sulphuric acid dissolved the tribromphenylene diamine at once, the solution having a purplish tint, which turned to dark brown if it was allowed to stand for some time, or if it was stirred in a current of air for a short time. Nevertheless on one occasion a white solid was obtained, but before it could be collected a black spot appeared in one part of it which spread rapidly through the whole mass. Dilute sulphuric acid had no apparent effect on it in the cold, but decomposed

[1] Ztschr. Chem. 1865, 555.

it when hot. These observations show that the presence of the three atoms of bromine has destroyed in great measure the basic properties of the phenylene diamine; but still it is possible to prepare salts of our substance, if proper precautions are observed, and the chloride is described somewhat later in this paper. Potassic hydrate, even when a boiling concentrated solution was used, produced no effect upon it.

When the tribromphenylene diamine is treated with tin and hydrochloric acid, it is converted into phenylene diamine. The details of this work are given later in this paper. The success of this experiment suggested to us that the bromine might be removed also by other reagents; accordingly we heated some tribromphenylene diamine dissolved in benzol and alcohol with sodic ethylate, the action in one trial being continued for four days, but at the end of this time we recovered nearly the whole of the tribromphenylene diamine taken, and although the filtrate after treatment with nitric acid and argentic nitrate gave a slight precipitate, we ascribe this rather to the complete decomposition of a small portion of the substance (indicated by the dark brown color of the product) than to any simple reaction. As therefore sodic ethylate had no action, it did not seem to us worth while to try other experiments with less energetic reagents.

Chloride of Tribromphenylene Diamine, $C_6HBr_3NH_2ClNH_2$.—Although the tribromphenylene diamine forms no salts under ordinary conditions, we hoped that we might obtain its chloride by the method which yielded such excellent results to Gattermann[1] when he applied it to the tribromaniline. Accordingly hydrochloric acid gas was passed into a solution of tribromphenylene diamine in benzol, until it ceased to form a white precipitate, and the liquid fumed strongly. The precipitate was then filtered out, and dried by pressing between filter paper as quickly as possible, after which it was analyzed as follows:

0.3096 gram of the salt lost 0.0272 gram of hydrochloric acid at 100°.

	Calculated for $C_6HBr_3NH_2ClNH_2$.	Found
Hydrochloric Acid	9.56	8.79

[1] Ber. d. chem. Ges., **16**, 636.

The residue was entirely free from hydrochloric acid. This result is not so near the theoretical percentage as could be wished, but nevertheless proves that the salt is a monochloride of tribromphenylene diamine. The poor result is undoubtedly to be ascribed to the instability of the compound, which lost as much as 3.3 per cent. of its weight by standing four days in a desiccator over sulphuric acid, and therefore might well have lost the 0.77 of one per cent during the drying on filter paper. The chloride as obtained was of a light brown color, although it is probably white when perfectly pure, and as indicated by the description of its analysis is very unstable, decomposing slowly in dry air at ordinary temperatures, quickly and completely when heated to 100°. We should judge that it is somewhat more stable than the chloride of tribromaniline prepared by Gattermann,[1] as might be expected from the presence of the second amido group. It seems to be soluble in strong hydrochloric acid since the tribromphenylene diamine dissolves in this reagent, but it is decomposed by water.

Tribromphenylene Diacetamide, $C_6HBr_3(NHC_2H_3O)_2$.—This substance was made by treating tribromphenylene diamine with acetyl chloride, using anhydrous benzol as a solvent. The action began even in the cold as shown by the deposition of a white precipitate, but to make certain that it was complete the mixture was heated under a return-condenser for one hour. At the end of this time the white sandy precipitate was filtered out, and purified by extraction with glacial acetic acid, followed by recrystallization from the same solvent boiling. It was dried at 100°, and analyzed with the following results:

I. 0.2726 gram of the substance gave 0.3561 gram of argentic bromide by the method of Carius.

II. 0.2548 gram of substance gave 0.3358 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHC_2H_3O)_2$.	Found. I.	II.
Bromine	55.94	55.59	56.08

Properties.—The tribromphenylene diacetamide crystallizes from hot glacial acetic acid in bunches of small white plates

[1] Loc. cit.

much longer than they are broad, which have square ends and frequently radiate from a centre; from alcohol in radiating groups of compound crystals made up of needles united longitudinally. It does not melt at 330°, and is very slightly soluble in all the common solvents. The best solvent for it is hot glacial acetic acid, but it is far from freely soluble even in this.

Tribromphenylene Diurethane, $C_6HBr_3(NHCOOC_2H_5)_2$.—Five grams of tribromphenylene diamine were boiled with about twice the amount of chlorocarbonic ester required by the theory in a return-condenser for three hours. The crude product (which weighed 6.5 grams), was purified at first by precipitating the substance with ligroïn from its solution in a mixture of benzol and alcohol, afterward by recrystallization from a mixture of alcohol and ligroïn, or alcohol and water, until it showed the constant melting-point 212°, when it was analyzed with the following results:

I. 0.3036 gram of the substance gave by the method of Carius 0.3454 gram of argentic bromide.

II. 0.1945 gram of the substance gave 0.2239 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHCOOC_2H_5)_2$.	Found. I.	II.
Bromine	49.08	48.42	48.99

Properties.—The tribromphenylene diurethane when deposited from alcohol forms very small crystalline masses, which under the microscope are seen to be rosettes made up of what at first sight appear to be short needles, but on closer examination prove to be groups of finer needles united longitudinally, since they betray their complex nature by the frayed or brush-like appearance of their ends, which resemble a partially untwisted cord. Its color is white, and it melts at 212°. It is soluble in cold alcohol, easily soluble in hot; easily soluble in chloroform, or acetone, less so in ether; somewhat soluble in cold benzol, easily soluble in hot, from which it crystallizes in the same form as from alcohol, but not so well; slightly soluble in carbonic disulphide even when hot; essentially insoluble in ligroïn. Water dissolves it to a very slight extent when hot. Hydrochloric acid produced no apparent effect

hot or cold; sulphuric acid did not act on it in the cold, but when hot dissolved it; from this solution it seemed to be precipitated unchanged by water, if the heating had not been long continued, but long heating with the strong acid decomposed it. A concentrated solution of potassic hydrate seemed to have no effect on it in the cold, but when heated turned the substance brown, and finally black with apparently complete decomposition. The best solvent for it is alcohol diluted with either water or ligroïn.

Reduction of Tribromdinitrobenzol.

Tribromdinitrobenzol (melting at 192°, made from symmetrical tribrombenzol) was reduced by treatment either with zinc and acetic acid, or with tin and hydrochloric acid, but the products were different in the two cases as described in the following sections.

Reduction with Zinc Dust and Acetic Acid.—This reduction we found it best to carry on in an atmosphere of carbonic dioxide, as the liquid showed a strong tendency to turn black during the process. The zinc dust contained in a flask kept full of carbonic dioxide was covered with acetic acid of 80 per cent., and the tribromdinitrobenzol added in small quantities at a time. If the zinc dust and tribromdinitrobenzol were mixed together before adding the acetic acid the action was far too violent; in fact, once the mixture took fire when the acetic acid was added. Even when the process was carried on as directed, the action was energetic at first, but later it was necessary to warm the flask gently to assist the reaction. The products were in part dissolved in the aqueous liquid, which with all our precautions, was invariably dark colored, and partly appeared as a crystalline powder in the bottom of the flask. The insoluble part was recrystallized from benzol, by which it was separated into a large fraction melting at 158°, a small amount of substance melting at a lower temperature, and a little unaltered tribromdinitrobenzol. The principal product was shown to be tribromphenylene diamine by its melting-point, but to confirm this it was dried at 100° and analyzed, when it gave the following results:

0.2337 gram of the substance gave by the method of Carius 0.3786 gram of argentic bromide.

	Calculated for $C_4HBr_3(NH_2)_4$.	Found.
Bromine	69.56	68.95

This percentage of bromine, although not agreeing with that calculated so closely as could be wished, is yet accurate enough when taken in connection with the melting-point to leave no doubt as to the nature of the substance formed, and therefore we did not attempt to get a number nearer to the theoretical.

The amount of tribromphenylene diamine formed by the reduction was considerable ; in one case 10 grams of tribromdinitrobenzol yielded 4.7 grams of it, and 0.9 gram of tribromdinitrobenzol were recovered unaltered, so that the percentage of the theoretical yield was 60.6. The remainder of the product was contained in the aqueous solution (and to a less extent in the small amount of lower-melting material from the benzol mother-liquors) ; it undoubtedly consisted of phenylene diamine, from which part or all the bromine had been removed, since the aqueous solution gave tribromphenylene diamine when treated with bromine water, a behavior which, as we have already stated, belongs to solutions of phenylene diamine and its salts.

Reduction with Tin and Hydrochloric Acid.—We found it best to proceed as follows : Some granulated tin with a piece of platinum and about 300 cc. of strong hydrochloric acid were gently warmed in a flask closed by a cork provided with a Bunsen valve, until the greater part of the air had been expelled. 10 grams of tribromdinitrobenzol mixed with enough alcohol to make a thick paste were then added, and the reduction was allowed to go on, warming or cooling the mixture as was necessary, until all the organic substance had dissolved. If the solution thus obtained was a strong one, beautiful white needles of a double tin salt were deposited on cooling ; if it was more dilute, they usually appeared after standing a day, but in some cases the substance obstinately refused to crystallize. The crystals were filtered out, and decomposed in concentrated solution with sulphuretted hydro-

gen, when the filtrate from the sulphide of tin left on evaporation a crystalline solid, which after three crystallizations from a mixture of water and hydrochloric acid, was analyzed with the following results:

I. 0.2220 gram of the substance gave 31.8 cc. of nitrogen at a temperature of 26°.5 and a pressure of 756.9 mm.

II. 0.2983 gram of the substance gave by the method of Carius 0.4727 gram of argentic chloride.

	Calculated for $C_6H_4(NH_3Cl)_2$.	Found. I.	II.
Nitrogen	15.47	15.79	....
Chlorine	39.21	....	39.17

The tin and hydrochloric acid had therefore reduced both the nitro groups, and also removed all three of the atoms of bromine from the tribromdinitrobenzol; and that the removal of bromine had taken place from the whole of the substance was made probable by the fact that all the organic matter dissolved, whereas the tribromphenylene diamine, as already stated in this paper, is insoluble in water or dilute hydrochloric acid. An additional confirmation of the presence of phenylene diamine was given by the following experiment. The base set free from the soluble chloride analyzed above was treated with bromine water, when a precipitate was formed, which after recrystallization from alcohol containing a little benzol, melted at 158°, and was therefore the tribromphenylene diamine which is made in this way from metaphenylene diamine.

When we began work on this subject we made many analyses of the double tin salt which crystallized out of the solution after the reduction; but although in two different preparations we obtained numbers agreeing with the salt $C_6H_4(NH_3ClSnCl_2)_2$, discovered by Gudemann,[1] we found that in others its composition varied so much that no certain inference in regard to the composition of the base formed could be drawn from these analyses, and therefore prepared the salt free from tin as described above.

After we had shown by the work just described that the three atoms of bromine are removed from tribromdinitroben-

[1] Ztschr. Chem., 1865, 51.

zol by tin and hydrochloric acid, it became of interest to determine whether their removal was due to the effect of the two nitro groups upon them. This seemed a probable supposition, because it has been repeatedly observed that atoms of bromine can be easily removed from the benzol ring when they stand in the ortho position to nitro groups, and work done in this laboratory has proved that this tribromdinitrobenzol is a very reactive body, but on the other hand it did not seem likely that the bromine atoms would be removed before the reduction of the nitro groups, as all previous experience seems to show that the latter are much more easily attacked than the former. It was obvious that this point could be decided by trying the action of tin and hydrochloric acid on tribromphenylene diamine, for none of the bromine would be removed from this substance if this action depended on the presence of the nitro groups. Accordingly five grams of tribromphenylene diamine were mixed with tin and hydrochloric acid and a piece of platinum added to increase the action. In the cold no change was observed, and therefore the mixture was warmed on the water-bath, when, after a vigorous reaction had gone on for a short time, all the organic matter dissolved. The brown clear solution deposited crystals as it cooled, but disregarding these the whole was treated with an excess of sodic hydrate and extracted with ether repeatedly. The residue from the ethereal extracts was an oil, which solidified after it had been scratched with a sharp glass rod, and then melted at about 62°. There was little doubt therefore that this substance was metaphenylene diamine, which melts at 63°, and this view was confirmed by the following observations. The substance gave a white salt with hydrochloric acid soluble in water, but nearly insoluble in hydrochloric acid. To a solution of this chloride bromine water was added, taking care to avoid an excess; this produced a white precipitate, which after recrystallization from benzol, melted at 158°, and was therefore tribromphenylene diamine. It follows from this experiment (which was repeated several times) that tribromphenylene diamine gives up all its bromine to tin and hydrochloric acid, and therefore that the re-

moval of the bromine atoms does not depend on the loosening effect of the two nitro groups.

Action of Tin and Hydrochloric Acid on Tribrombenzol and on Tribromaniline.—After we had shown, as just described, that all the bromine can be removed from tribrommetaphenylene diamine by the action of tin and hydrochloric acid, it occurred to us that the comparatively loose attachment of the bromine to the benzol ring might be due to the fact that the three atoms of bromine were in the symmetrical position, since Blau has shown that one of these atoms in tribrombenzol can be replaced by the methoxy radical, and we have confirmed this observation. This hypothesis seemed the more probable because dibrommetaphenylene diamine is reduced under these conditions much more slowly than the tribrom compound. If this view is correct, tin and hydrochloric acid should remove bromine from the symmetrical tribrombenzol, and accordingly we tried the following experiment. Ten grams of tribrombenzol were mixed with granulated tin and strong hydrochloric acid, a piece of platinum added to promote the action, and enough alcohol to dissolve a large part of the tribrombenzol. The reason for adding the alcohol was that we thought the action of the reducing agent on the tribrommetaphenylene diamine might be in part due to its tendency to dissolve in the acid, or still more to the solubility of the products of the reduction in the acid, and we hoped by the addition of the alcohol to establish similar favorable conditions in the case of tribrombenzol. The mixture was heated under a return condenser over the water-bath for a week. At the end of this time enough water was added to precipitate any brombenzols which might be present, and the heavy crystalline precipitate thus obtained was filtered, and washed until it was free from stannous chloride. It was then dried and weighed, when 9.5 grams were obtained, so that the loss was no greater than would be expected from the rough way in which the experiment had been carried on. This substance melted at 120°, and was therefore unaltered tribrombenzol (melting-point 119°.6). It follows from this experiment that tin and hydrochloric acid do not remove bromine from symmetrical tribrombenzol, and, therefore, that the conversion of

tribrommetaphenylene diamine into metaphenylene diamine by these reagents is not due to the symmetrical position of the bromine atoms, although it may have a subsidiary effect in assisting this conversion.

An experiment similar to that just described was tried with 10 grams of tribromaniline. The conditions were exactly the same as those used for tribrombenzol, given at length in the preceding paragraph. Upon adding water to precipitate the organic substances, after the reduction was completed, only a very small precipitate was formed, which in time changed to long needles. This precipitate weighed less than 0.5 gram, and as it melted at 118° was undoubtedly unaltered tribromaniline. The filtrate from this precipitate was treated with an excess of sodic hydrate, the precipitate thus formed dissolved in hydrochloric acid, and reprecipitated with sodic hydrate in excess to remove the hydrate of tin as completely as possible, and then extracted with alcohol. The alcoholic extract deposited long white needles, which melted at 78–79°, and were therefore probably dibromaniline. To establish the nature of the substance more fully, we tried the following experiments. The amido group was replaced by bromine, when a product was obtained melting at 44°, the melting-point of the unsymmetrical tribrombenzol, and this when treated with nitric acid, was converted into the mononitrotribrombenzol, melting at 93°. There can be no doubt therefore that the tin and hydrochloric acid have removed one of the atoms of bromine from the ortho position to the amido group, replacing it by hydrogen. A quantitative experiment gave the following results: 10 grams of symmetrical tribromaniline yielded after reduction for six hours, 5 grams of dibromaniline, from which were obtained 5 grams of unsymmetrical tribromaniline, and from this 5.2 grams of tribromnitrobenzol.

Dibrommetaphenylene Diacetamide, $C_6H_2Br_2(NHC_2H_3O)_2$.

Whereas free metaphenylene diamine gives a tribrom derivative when treated with bromine water, we have obtained only the dibrom compound from metaphenylene diacetamide, even when a considerable excess of bromine was used. The samples analyzed were prepared by the method given below,

but a better method discovered later is described after the analyses: Metaphenylene diacetamide was dissolved in common acetic acid with the aid of gentle heat, and treated at first with bromine, and afterward with bromine water, until a slight excess had been added. The new substance separated from the solution as it was formed, and after standing a short time it was filtered out, and purified by crystallization from hot glacial acetic acid until it showed the constant melting-point 259°, when it was dried at 100° and analyzed with the following results:

I. 0.2471 gram of the substance gave 19 cc. of nitrogen at a temperature of 29° and a pressure of 754.3 mm.

II. 0.2145 gram of the substance gave by the method of Carius 0.2294 gram of argentic bromide.

III. 0.2033 gram of the substance gave by the method of Carius 0.2198 gram of argentic bromide.

	Calculated for $C_4H_2Br_2(NHC_2H_3O)_2$.	Found. I.	II.	III.
Nitrogen	8.00	8.33	....	....
Bromine	45.71	....	45.52	46.01

The substance can be obtained more expeditiously in a pure state by avoiding the preparation of solid phenylene diacetamide as follows: A strong ethereal solution of phenylene diamine is treated with acetic anhydride until a portion gives a white or yellow precipitate with bromine (if unaltered phenylene diamine is present the precipitate will be brown). When this is the case an excess of bromine water is added to the solution, and the mixture stirred vigorously until the precipitation is complete. The product is essentially pure without recrystallization.

Properties.—The dibrommetaphenylene diacetamide crystallizes by slow evaporation from an alcoholic solution in very small, rather short prisms. If on the other hand the crystallization takes place by cooling, obscurely crystalline masses are obtained in which it is hard to make out any definite form; they seem to be prisms coated with needles. Its color is white, and it melts at 259° to 260° with decomposition, as is shown by the fact that the melted mass turns black and puffs up to many times its original volume. On account of this

decomposition it is necessary to keep the melting-tube in the oil bath as little as possible in determining the melting-point. If the substance is allowed to remain in the bath while its temperature is raised, a melting-point as low as 250° may be obtained. It is very slightly soluble in cold alcohol, and only a little more soluble in hot; very soluble in benzol, chloroform, or carbonic disulphide; somewhat more soluble in acetone or glacial acetic acid; essentially insoluble in ether or ligroïn. The best solvent for it is glacial acetic acid or alcohol, although it is soluble in the latter only sparingly and with great difficulty. It is very slightly soluble in boiling water, insoluble in cold. Strong hydrochloric acid saponifies it quickly when the two are gently heated together; strong sulphuric acid dissolves it in the cold, but without decomposition, as the unaltered substance is obtained by diluting and neutralizing the acid; it decomposes the substance when hot; if dilute it has no apparent effect when cold, but when heated saponifies and afterward decomposes it; strong nitric acid dissolves it quickly when cold, but the substance is recovered unaltered on neutralization; when hot it decomposes it. A strong solution of potassic hydrate saponifies it when hot.

Dibrommetaphenylene diamine. $C_6H_2Br_2(NH_2)_2$.—This substance was obtained by removing the acetyl groups from the preceding compound as follows: 10 grams of the dibromphenylene diacetamide were heated with from 30 to 40 cc. of commercial strong hydrochloric acid for half an hour in a flask with a return-condenser; at the end of this time the solid was completely dissolved, and the liquid had taken on a dark brownish-red color. After it was cold the solution was treated at first with sodic carbonate, and finally with sodic hydrate in excess, which precipitated a brown solid. This was filtered out, washed until free from alkali, and purified by crystallization from boiling water containing a little alcohol, until it showed the constant melting-point 135°. In this recrystallization long heating of the solution should be avoided, as this seems to decompose the substance with precipitation of a black compound. The pure substance was dried at 100° and analyzed with the following result:

0.3872 gram of the substance gave by the method of Carius 0.5473 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Bromine	60.15	60.16

Properties.—The dibromphenylene diamine crystallizes in fine needles which are white if the substance is perfectly pure, but usually show a brownish color, which is due to an impurity so slight that it has no effect upon the analysis. It melts at 135°, and is easily soluble in alcohol whether hot or cold. It is very soluble in acetone; easily soluble in ether, somewhat less soluble in benzol, or chloroform, if cold, easily soluble if hot; slightly soluble in cold carbonic disulphide, soluble when hot; very slightly soluble in cold ligroïn, more soluble when it is hot; nearly insoluble in cold water, slightly soluble in hot, but it is decomposed if boiled for some time with water. The best solvent for it is dilute alcohol. It shows a much stronger tendency to form salts than the tribromdiamine, as it dissolves in either hydrochloric acid or hydrobromic acid, and the solution leaves the salt on spontaneous evaporation; cold strong sulphuric acid turns it purple and then dissolves it, but on standing the sulphate separates from this solution in glistening white or pinkish plates, which seem to belong to the monoclinic system; when hot, sulphuric acid decomposes it; strong nitric acid dissolves it, and then decomposes it even in the cold, forming a brown solution. A cold solution of potassic hydrate has no effect upon it, but, if the mixture is heated, decomposition sets in as is shown by the appearance of a black color. We selected for further study the chloride and the bromide of the base with the results described below.

We have also studied the action of tin and hydrochloric acid on the dibromphenylene diamine. For this purpose 3.75 grams of the dibromphenylene diamine were warmed with tin, hydrochloric acid, and platinum under the conditions already described when speaking of the tribromphenylene diamine. The action in this case was very slow; whereas the tribrom compound dissolved after treatment for a short time, it was necessary to carry on the action for over twelve hours in order

to bring the dibromamine into solution. The product yielded an oily free base, smelling like metaphenylene diamine, which, however, we did not succeed in obtaining in a solid state. It gave an easily soluble chloride, so there can be no doubt that bromine was removed. We were unable to determine with certainty the cause of the very slow removal of the bromine from the dibromphenylene diamine; it is possible that it is only mechanical, as it was observed that this substance showed a tendency to form a coating on the surface of the tin, or on the other hand it may be that the symmetrical position of the three atoms of bromine in the tribromphenylene diamine has the effect of loosening their attraction for the benzol ring. The latter explanation seems to us the more probable.

Chloride of Dibromphenylene Diamine, $C_6H_2Br_2NH_2ClNH_2$. —This salt can be made by dissolving the diamine in strong aqueous hydrochloric acid and allowing the solution to evaporate spontaneously, but we did not use this method in preparing the salt for analysis, because we feared it might undergo a partial decomposition, if deposited from a solution containing water. We therefore prepared it by passing hydrochloric acid gas through a solution of the diamine in benzol, until the liquid fumed strongly, and no more solid matter was deposited. The precipitate thus obtained was pressed repeatedly between filter paper, and dried for one hour over sulphuric acid, when it gave the following result on analysis:

0.2173 gram of the salt gave by the method of Carius 0.3713 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6H_2Br_2NH_2ClNH_2$.	Found.
Chlorine and bromine	64.63	64.28

The chloride of dibromphenylene diamine is much more stable than the corresponding tribrom compound, since, whereas the chloride of tribromphenylene diamine lost all its hydrochloric acid when heated to 100° for a short time, the chloride of dibromphenylene diamine showed a loss under the same conditions of only 5 per cent. instead of the 12.07 per cent., which represents the loss, if the whole of its hydrochloric acid had been given up. Further, the salt of the di-

brom compound can be made by the action of a strong aqueous solution of hydrochloric acid upon the free base, while, although the tribrom base dissolves in strong hydrochloric acid, we have not succeeded in obtaining the solid chloride from this solution. It must not be inferred from this comparison, however, that the choride of dibromphenylene diamine is especially stable, for this is not the case, since it loses nearly 4 per cent. of its weight by standing in a desiccator, and is also decomposed by water.

Bromide of Dibromphenylene Diamine, $C_6H_2Br_2NH_2BrNH_2$. —This substance was made by adding dibromphenylene diamine to distilled hydrobromic acid (boiling-point 123°) until it ceased to dissolve easily in the cold. A good deal of trouble was encountered in obtaining the solid salt from this solution, as heating decomposed it, and none of the organic solvents miscible with water gave a precipitate with it; spontaneous evaporation indeed gave the salt, but as we did not know its properties at the time of the preparation we were afraid of decomposition during such long standing, and accordingly proceeded as follows: The aqueous solution was covered with a rather thick layer of ether, and the whole stirred vigorously for about a quarter of an hour; under this treatment the bromide crystallized out in the lower part of the ether, when it was separated, washed with ether, and dried in a desiccator over sulphuric acid. It then gave the following results on analysis:

I. 0.4433 gram of the substance gave by the method of Carius 0.7191 gram of argentic bromide.

II. 0.3014 gram of the substance gave 0.4884 gram of argentic bromide.

	Calculated for $C_6H_2Br_2NH_2BrNH_2$.	Found. I.	II.
Bromine	69.16	69.04	68.96

The sample used for the first analysis had been dried for only three hours, and for the second had stood in a desiccator over sulphuric acid for three days, showing that the salt is stable under these circumstances. The bromide is therefore more stable than the chloride, as that lost nearly 4 per cent.

of its weight in a desiccator, which amounts to one-third of the acid that it contains.

The bromide of dibromphenylene diamine forms white needles, which turn brown quickly, when exposed to the air. It is decomposed by water, but is soluble in ethyl, or methyl alcohol, the solution apparently decomposing on standing; insoluble in ether, benzol, or ligroïn.

Reduction of Tetrabromdinitrobenzol.—The tetrabromdinitrobenzol was prepared essentially by the method given by Bancroft and one of us,[1] but a few improvements in the process should be mentioned here. By using a large amount of glacial acetic acid the yield of tetrabrombenzol was materially raised. The details of this process will be found in our paper, "On the Behavior of Certain Halogen Derivatives of Benzol." In converting the tetrabrombenzol into the dinitro compound we found that the quantities of sulphuric acid and nitric acid used could be reduced to 50 cc. of each for 10 grams of tetrabrombenzol, if the tetrabrombenzol was pure; if this was not the case the best method was to treat the tetrabrombenzol with the acid mixture, which had already been used once with tetrabrombenzol; the product of this action of the residual acid was then treated with one-half the amount of fresh sulphuric acid and nitric acid needed for the complete conversion of the tetrabrombenzol into the dinitro compound, and in this way a nearly pure product was obtained at little expense of fuming nitric acid. With pure tetrabrombenzol the yield was very nearly quantitative, 100 grams giving 121 grams of a product melting at 220°, which, after one recrystallization, melted at 227°, the correct melting-point for tetrabromdinitrobenzol; as 100 grams should give 122.8 grams, this makes the yield of this crude product over 99 per cent.

To reduce the tetrabromdinitrobenzol it was mixed with alcohol, tin, and hydrochloric acid, and the mixture heated on the water-bath in a flask with a return-condenser, more hydrochloric acid being added from time to time. When the volume of liquid became unpleasantly large, it was evaporated in an open dish to a convenient volume, and returned

[1] This JOURNAL, 12, 290.

to the flask with fresh alcohol and acid. After the organic matter had gone completely into solution, which usually happened after boiling for about seventy hours, the liquid was again concentrated and rendered strongly alkaline with crude sodic hydrate. The hydrate of tin was filtered out with cheese-cloth, and dried as thoroughly as possible by sucking air through it, after which it was shaken repeatedly with rather large amounts of alcohol. The alcoholic extract thus obtained was freed from alcohol by distillation, followed by evaporation on the water-bath, when an oil and an aqueous solution were left, which were separated, if possible, mechanically; if not, by shaking with ether. The oil obtained directly or from the ether solidified after a short time. The aqueous filtrate from the hydrate of tin with the liquid separated from the oil was shaken with ether repeatedly, and the oil thus obtained added to the main portion. The aqueous solution, after shaking with ether, gave a very slight precipitation on the addition of bromine, but the amount of tetrabromphenylene diamine obtained in this way was so small that this treatment is hardly worth while. The principal product, after it had solidified, was purified by dissolving it in rather dilute alcohol and saturating the solution with sulphuretted hydrogen, when it was warmed gently, and allowed to stand in a corked flask for some time; after filtering off the sulphide of tin it was evaporated to dryness, and the residue recrystallized from pure ligroïn (boiling from 60–70°) until it showed the constant melting-point 93–94°, when it was dried in a desiccator and analyzed with the following result:

0.2117 gram of the base gave by the method of Carius 0.2113 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_2)_2$.	Found.
Bromine	42.79	42.48

Properties of Monobrommetaphenylene Diamine.—It crystallizes from a mixture of benzol and ligroïn in white spindle-shaped forms often a centimeter long; from benzol alone in bundles of small needles united longitudinally; from alcohol in not very well developed prisms apparently belonging to the monoclinic system and often twinned. It melts at 93–94°,

and is readily soluble in acetone, alcohol, ether, or chloroform; in benzol, or carbonic disulphide it is slightly soluble in the cold, more freely when hot; nearly insoluble in cold ligroïn, difficultly soluble in hot; it is moderately soluble in cold water, as shown by the fact that such a solution gives a good precipitate with bromine water, in hot water it is even more soluble, the solution as it cools depositing oil drops, which later change to needles. The best solvent for it is a mixture of benzol and ligroïn, but crystallization from pure ligroïn is necessary to get a perfectly white product. It shows a tendency to separate from its solutions at first as an oil, and also to become decomposed, when in solution, forming a brown product.

The monobromphenylene diamine shows marked basic properties. Hydrochloric acid or hydrobromic acid gives with it a salt soluble in water, a description and analysis of the bromide formed in this way is given below; moderately strong sulphuric acid also gives a soluble salt, which forms white crystals when the solution is allowed to evaporate spontaneously; dilute nitric acid seems to have little action on it in the cold, but when hot converts it into a brown substance. Sodic hydrate seems to have no action even when warmed with it for several minutes on the water-bath. The constitution of the monobromphenylene diamine is probably $NH_2.H.NH_2.H.Br.H$, as the tribromdinitrobenzol made from symmetrical tribrombenzol loses all its bromine when reduced under the conditions used in obtaining the monobromphenylene diamine from tetrabromdinitrobenzol.

Bromide of Monobromphenylene Diamine, $C_6H_3Br(NH_2Br)_2$.—Monobromphenylene diamine was mixed with distilled hydrobromic acid (boiling-point 124–125°), and the liquid heated to boiling. The solid was then brought into solution by the careful addition of just the proper amount of water to the boiling solution, after which more of the hydrobromic acid was added, until crystallization began, when the mixture was allowed to cool. The crystals thus obtained were washed with hydrobromic acid and then with ether, dried by pressure with filter-paper, and washed with ether a second time. After

drying over sulphuric acid the salt was analyzed with the following result:

0.2474 gram of the substance gave according to the method of Carius 0.3945 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_3Br)_2$.	Found.
Bromine	68.77	67.86

This analysis leaves much to be desired, but the result is near enough to show that the formula given above is correct. The salt forms colorless, transparent, glassy crystals, which look like cubes under the microscope; freely soluble in water, slightly in hydrobromic acid.

Tetrabromphenylene Diamine, $C_6Br_4(NH_2)_2$.—This substance was made by dissolving the monobromphenylene diamine, melting at 93–94° in ether, and adding a slight excess of bromine; the product, after recrystallization from a mixture of chloroform and ligroïn, showed the constant melting-point 212–213°, when it was dried and analyzed with the following result:

I. 2357 gram of the substance gave by the method of Carius 0.4166 gram of argentic bromide.

II. 0.2493 gram of the substance gave 0.4432 gram of argentic bromide.

	Calculated for $C_6Br_4(NH_2)_2$.	Found. I.	Found. II.
Bromine	75.47	75.22	75.67

Properties of Tetrabromphenylene Diamine.—It crystallizes in very small white needles, which melt at 212–213°, and are freely soluble in benzol, chloroform, ether, acetone, or carbonic disulphide; slightly soluble in cold alcohol, freely in hot; almost insoluble in cold ligroïn, slightly soluble in hot. The best solvent for it is a mixture of chloroform or benzol with ligroïn. The tetrabromphenylene diamine has nearly, if not quite, lost the basic properties of a diamine, as was to be expected, since it is loaded with so many negative bromine atoms. Hydrobromic acid had but little apparent action on it, even when hot, although the liquid deposited after long standing a few transparent crystals, which may have been the bromide.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON BENZIMIDOETHYL AND BENZIMIDOMETHYL ETHERS.

By F. W. Bushong.

In connection with a study of imidomethyl carbonate, cyanimidomethyl carbonate and other imido ethers,[1] undertaken at the suggestion of Dr. J. U. Nef, it was considered of interest to study the properties of benzimido ethers. Pinner[2] has described a large number of hydrochloric acid addition-products of the imido ethers, but he has in only a few cases briefly mentioned the free ethers as being very unstable products, which he was unable to obtain in a pure state. Thus, for example, he describes benzimidoethyl ether as an oil which on standing, or more quickly on heating to 100°, decomposes into alcohol and cyanphenin.

Wheeler[3] has more fully described benzimidomethyl ether and its behavior, especially towards aromatic ortho compounds, but he makes no attempt to purify or analyze the crude reaction-product.

Benzimidoethyl ether, $C_6H_5C\begin{matrix}\diagup NH\\ \diagdown OC_2H_5\end{matrix}$.—By passing dry hydrochloric acid gas into benzonitril and alcohol, according to the method of Pinner,[4] the crystalline addition-product, $C_6H_5—\begin{matrix}\diagup Cl\\ NH_3\\ \diagdown OC_2H_5\end{matrix}$, was prepared. This was powdered, washed with absolute ether and dried in a vacuum; 9.25 grams of the dry salt were gradually added to 100 cc. of a 10 per cent. solution of caustic soda, which was cooled by a freezing-mixture. The oil, which separated out, was immediately extracted with ether, and dried with calcium chloride; after distilling off the ether, an oil was obtained which boiled at 106–9° at 15 mm. pressure; redistilled at ordinary pressure, it boiled absolutely constant at 218°, without the slightest decomposition, as shown by the analysis.

I. 0.2081 gram substance gave 0.5504 gram CO_2 and 0.1460 gram H_2O.

1 Nef: Ann. Chem. (Liebig), **287**, 265-360.
2 "Die Imidoaether und ihre Derivate."
3 This Journal. **17**, 397. 4 Ber. d. chem. Ges., **16**, 1654.

II. 0.3456 gram substance gave 29.6 cm. N_2 at 18°, and 749.3 mm.

	Calculated for $C_9H_{11}NO$.	Found.
C	72.48	72.13
H	7.38	7.78
N	9.40	9.75

Benzimidomethyl ether, $C_6H_5C\begin{matrix}=NH\\ \diagdown OCH_3\end{matrix}$.—In like manner benzimidomethyl ether was prepared from benzonitril and methyl alcohol. It was found to boil at 96° at 10 mm., and 206° at ordinary pressure.

I. 0.2148 gram substance gave 0.5621 gram CO_2, and 0.1246 gram H_2O.

II. 0.2054 gram substance gave 18.3 cm. N_2 at 17°.5 and 750.5. mm.

	Calculated for C_8H_9NO.	Found.
C	71.11	71.37
H	6.66	6.43
N	10.37	10.18

Both ethers are colorless mobile liquids, quite stable when pure and dry, and have a peculiar pleasant odor; they can be kept for months without change. I have not only verified the statement of Wheeler that the methyl ether does not solidify at —30°, but have been unable to solidify the ethyl ethers at the same temperature.

ON THE HALOGEN DERIVATIVES OF THE SULPHONAMIDES.

By J. H. Kastle, B. C. Keiser, and Ernest Bradley.

Some months ago there appeared[1] a preliminary notice by one of us (Kastle) ot the halogen derivatives of the sulphonamides, in which it was proposed to use one of these derivatives, *viz.*, benzenedichlorsulphonamide, $C_6H_5SO_2NCl_2$, as a reagent for bromine and iodine. Attention was therein called to the rather unsatisfactory condition of our knowledge regarding similar derivatives of the amides of the carbonic acids; and consequently to the advisability of making further studies of this class of compounds. For some

[1] This Journal, 17, 104.

months past investigations along this line have been conducted in this laboratory with the results recorded below.

Chlorine Derivatives.

Benzenedichlorsulphonamide, $C_6H_5SO_2N.Cl_2$.—This compound was prepared by leading into the solution of benzenesulphonamide in the smallest possible quantity of caustic soda (1–10) a rapid current of chlorine gas. Under these conditions a copious, white, crystalline precipitate was thrown down. This was filtered off and purified by heating the precipitate with water, when the chlorine derivative melts to a heavy oil, and any unchanged amide dissolves. The hot water was poured off from the heavy oil, and the latter substance poured into cold water, when it solidified to a crystalline mass, closely resembling a solid sulphonchloride. The crystalline mass was then pulverized in a porcelain mortar and dissolved in the smallest quantity of alcohol in which it would dissolve. To this alcoholic solution water was added immediately, drop by drop, as long as any precipitate was produced. Under these conditions the dichlorsulphonamide was obtained in pearly white laminæ, which, in general appearance, greatly resemble the original amide. Looked at in considerable quantity the compound has a distinct greenish-yellow color, due to the presence of free chlorine. It is also exceedingly difficult to obtain the compound so that it does not possess a slight odor of either chlorine or a sulphonchloride, or of both. The reason of this will be discussed in a subsequent part of the paper. The benzenedichlorsulphonamide melts sharply at 70° C. to a clear, slightly yellowish oil. Heated in quantity to 218–220° C. it explodes. At 150° C. and over, it begins to decompose with evolution of chlorine gas and the formation of benzenesulphonchloride. It acts readily as an oxidizing agent yielding the amide among the other products of oxidation. Treated with strong acids such as hydrochloric or hydrobromic acid, it gives off chlorine, and the amide is produced. It gave the following numbers on analysis :

	Found. Per cent.	Calculated for $C_6H_5SO_2N.Cl_2$. Per cent.	Calculated for $C_6H_5SO_2NH_2Cl_2$. Per cent.
Hydrogen	0.26	0.22	0.30
Chlorine[1]	31.02	31.35	31.14

The results of this and the other analyses of the other compounds described in this paper will be discussed in a subsequent portion.

p-Toluenedichlorsulphonamide, $C_6H_4<^{CH_3}_{SO_2NCl_2(p)}$. — This compound was prepared by the same method as that above described, *i. e.*, by dissolving the *p*-toluenesulphonamide in the smallest possible quantity of caustic soda solution (1–10), and passing a rapid current of chlorine gas into the solution. Like the benzene compound it can be purified by heating with water and recrystallizing from alcohol by the addition of small quantities of water to the alcoholic solution. It resembles the corresponding benzene compound very closely. It tends to crystallize in rather smaller crystals, and it is rather more difficult to dry it and get it in pure condition. In its odor it strongly suggests a sulphonchloride, into which it doubtless decomposes as does the corresponding benzene compound. The toluene compound melts at 80° C. and explodes at high temperatures. Unfortunately the results of the determination of the amount of chlorine in this compound have been misplaced. From its characteristic properties there can be no doubt as to its nature.

p-Brombenzenedichlorsulphonamide, $C_6H_4<^{SO_2N.Cl_2}_{Br(p)}$.—This compound was prepared like the two compounds already described. When purified by dissolving in alcohol and precipitating with small quantities of water, it was obtained as a white crystalline powder possessing the odor of chlorine. It was found to melt at 106° C. It gave the following number for chlorine on analysis :

	Found.	Calculated for $C_6H_4<^{SO_2NH_2Cl_2}_{Br}$.	Calculated for $C_6H_4<^{SO_2N.Cl_2}_{Br}$.
	Per cent.	Per cent.	Per cent.
Cl	23.36	23.1	23.25

[1] The halogen in all of the compounds herein described was determined by boiling the compound in water with zinc dust, filtering, and titrating with one-tenth normal silver nitrate and ammonium sulphocyanide.

Bromine Derivatives.

Benzenedibromsulphonamide, $C_6H_3SO_2N.Br_2$.—This compound was obtained as a yellow crystalline precipitate by adding bromine or bromine water to a caustic soda solution (1–10) of the amide. On adding the bromine it sometimes happened that a lighter yellow compound was obtained—a substance doubtless of the nature of a double salt of this composition—$C_6H_3SO_2NBr_2NaBr$. By adding an excess of bromine or by simply allowing this double salt to stand under water, the sodium bromide was removed and the dibromsulphonamide obtained. It is possible to precipitate it out of an alkaline solution of the amide in pure state; if not so obtained it may be purified; like the corresponding chlorine compound, by dissolving it in alcohol and precipitating it out with small quantities of water, when it is obtained in dark yellow laminæ, which somewhat resemble lead iodide. The pure bromine compound melts at 110° C. with decomposition and evolution of bromine. Heated suddenly it explodes, bromine being evolved. The compound is almost or quite insoluble in cold water but is slightly soluble in hot water. It dissolves readily in alcohol, ether, chloroform, and carbon bisulphide. Several specimens of the compound gave the following numbers on analysis:

Specimen I, recrystallized from water, gave 50.65 per cent. Br.
" II, " " " " 50.42 " " "
" III, " " benzene and then from chloroform gave 49.07 per cent. Br.

	Calculated for $C_6H_3SO_2NH_2Br_2$. Per cent.	Calculated for $C_6H_3SO_2N.Br_2$. Per cent.
Bromine	50.47	50.79

p-Chlorbenzenedibromsulphonamide, $C_6H_4<^{SO_2N.Br_2}_{Cl(p)}$.—This compound was the first of the halogen derivatives of the sulphonamides obtained. It has already been briefly described in the preliminary notice above referred to. As therein stated, it was prepared by adding bromine water to a caustic soda solution of *p*-chlorbenzenesulphonamide. The substance thus obtained was crystalline, yellow in color, possessed a

slight odor of bromine, and gave the following numbers on analysis:

	Found.	Calculated for $C_6H_4<^{SO_2NH_2Br_2}_{Cl(p)}$.	Calculated for $C_6H_4<^{SO_2N.Br_2}_{Cl(p)}$.
	Per cent.	Per cent.	Per cent.
Bromine	45.53	45.51	45.78
Nitrogen	3.80	3.98	4.00
Sulphur	9.10	9.10	9.15

The attempt was also made to prepare the dibromine derivatives of a few other sulphonamides but without success. With *p*-brombenzenesulphonamide in alkaline solution, bromine and bromine water give a pasty yellow mass, which it was difficult to purify and crystallize, and which rapidly loses bromine on exposure to the air. The compound was not obtained sufficiently pure for analysis. It may be well to note in this connection that no such difficulty was encountered in the preparation of the chlorine compound; in fact the tendency to form such chlorine derivatives might almost be described as characteristic, at least of the sulphonamides of the benzene series.

According to Linebarger,[1] iodine substitution-products of the carbonic amides are impossible. Such would also seem to be the case with the sulphonamides. No such derivative has as yet been prepared, although several attempts have been made in this direction. We might reasonably expect that such a compound could be prepared by bringing the chlorine or bromine compound into a solution of potassium iodide. No such compound, however, is obtained, but in its stead compounds, crystallizing in plates, having a greenish bronze-like luster, which seem to have the nature of periodides of the sulphonamides, somewhat similar, doubtless, in composition and properties to the periodides of the sulphonates described by Kastle and Hill.[2] These compounds are still under investigation. Among other interesting properties they give up by far the greater portion of their iodine when boiled with water, or when dissolved in chloroform or carbon bisulphide, and it is in consequence of this latter property that we can use the dichlor derivatives of the sulphonamides in

[1] This JOURNAL, **16**, 216. [2] This JOURNAL, **16**, 116.

testing for iodine, as previously described in the preliminary notice above referred to.

Theoretical.

In the preliminary notice above referred to attention was called to the fact that but little seemed to be known whereas a good deal seemed to be taken for granted regarding the nature of the halogen derivatives of the sulphonamides. From what is known regarding the variable valence of nitrogen, and when it is borne in mind that the amides are very closely related to ammonia, it would not be far-fetched to imagine the existence of both substitution- and addition-products among the halogen derivatives of acid amides. From a theoretical standpoint such compounds as $C_6H_5SO_2N.Cl_2$ and $C_6H_5SO_2NHCl$ might exist, in which the nitrogen remained trivalent; or such compounds as $C_6H_5SO_2NH_2Cl_2$ and $C_6H_5SO_2NH_2.HCl$ in which the nitrogen has become quinquivalent as in the ammonium salts. To the former class of compounds have been relegated all the halogen derivatives of the carbonic amides[1] thus far discovered; whereas, in the latter class have been placed the halogen addition-products of the alkyl amides recently described by Remsen and Norris,[2] and also certain derivatives of the acid anilides which have lately been described by Wheeler and Walden.[3] The question, therefore, naturally suggests itself, to which of these two classes of nitrogen derivatives do the compounds described in the first part of this paper belong? Are these compounds substitution- or addition-products of the sulphonamides? These questions can, of course, only be answered through the study of the composition and chemical conduct of the compounds. Unfortunately, the differences in composition between such addition- and substitution-products are not sufficiently great to warrant a conclusion, as to the nature of these substances, from the analytical data alone. For example, the bromine addition-product of benzenesulphonamide, $C_6H_5SO_2NH_2Br_2$, contains 50.47 per cent. of bromine, whereas, the corresponding substitution-product contains 50.79 per cent. of bromine. Hence, if a compound, on analysis, were found to

[1] Ber. d. chem. Ges., **15**, 407; and **19**, 2274.
[2] This JOURNAL, **18**, 90. [3] *Ibid*, **18**, 85.

contain 50.65 per cent. of bromine, as was nearly the case, it would agree within the limits of experimental error with either of the above compounds, and, hence, something more than the quantity of bromine would have to be known before the nature of this compound could be made out. It is true that in most instances the quantities of chlorine or bromine are a little lower than the quantities required by the theory for the substitution-products; and, hence, agree better as a whole with the theoretical numbers for the addition-products. It should be borne in mind, however, in this connection, that these compounds are somewhat unstable, decomposing into acid chlorides and giving off small quantities of chlorine or bromine even at ordinary temperature. The chemical conduct of these derivatives towards a good many of the simple reagents has been studied, and has been found to be such as to suggest that they are substitution- rather than addition-products of the sulphonamides. That such is indeed the case may be seen from the following:

1. It has been observed that, when these substances are rapidly heated, they explode with evolution of the halogen. In this respect, at least, these compounds show an analogy to nitrogen trichloride, NCl_3, which is suggestive. Further, if these substances really be addition-products, such as $C_6H_5SO_2NH_2Cl_2$, and at the same time explosive, then it is difficult to understand why the chlorine should not come off in combination with hydrogen as hydrochloric acid, instead of in the free state. If, however, we regard the compound, $C_6H_5SO_2N.Cl_2$, as analogous to nitrogen trichloride, then, inasmuch as it contains so much chlorine in direct combination with the nitrogen, it ought to prove explosive and chlorine ought to be given off in the explosion. Again, it has been observed that, when the dichlorine derivative of benzenesulphonamide is slowly heated and kept at 170° C. for several hours, it decomposes with evolution of chlorine, nitrogen, and a little hydrochloric acid gas and benzenesulphonchloride is formed. It is certainly difficult to understand how such a reaction as this is possible with an addition-product such as $C_6H_5SO_2NH_2Cl_2$. Certainly, if the decomposition were sufficiently deep-seated actually to remove the nitrogen

from the compound, then the chlorine ought to come off in combination with the hydrogen as hydrochloric acid gas. Or, in the event that the nitrogen did not escape as a gas, it would not be very far-fetched to suppose the formation of ammonium chloride as one of the products of such a decomposition. No ammonium salt, however, was found in the residue, and only small amounts of hydrochloric acid were formed as compared with the free chlorine. On the other hand, if the decomposition with which we are here dealing be one of the substitution-product, $C_6H_4SO_2N.Cl_2$, then the reaction is not so difficult to understand. It would probably take place in the sense of this equation :

$$C_6H_4SO_2N.Cl_2 = C_6H_5SO_2Cl + N + Cl.$$

The small quantity of hydrochloric acid probably resulting from the action of a part of the nascent chlorine on the phenyl portion of the benzenesulphonchloride.

2. Strong acids act upon the halogen derivatives of the sulphonamides with great ease—setting free the halogen, and forming the corresponding amide. For example, a quantity of the bromine compound of benzenesulphonamide was heated with concentrated hydrochloric acid. Bromine was rapidly evolved and, on evaporating the liquid, and cooling, a white substance was obtained which, upon recrystallization from hot water, was found to possess all of the physical characteristics of benzenesulphonamide. It was found to melt at 152 C., and gave a beautiful yellow precipitate of the original bromine compound on treatment with bromine in alkaline solution. In the same way the chlorine derivative of *p*-brombenzenesulphonamide gave off chlorine abundantly when treated with concentrated hydrochloric acid with the formation of the original amide of *p*-brombenzenesulphonic acid; and, in like manner, bromine was evolved and benzenesulphonamide obtained when the benzenedibromsulphonamide was treated with hydrobromic and with nitric acid. It is difficult to see how acids would act upon addition-products, such as $C_6H_4SO_2NH_2Br_2$. On the other hand, just as nitrogen trichloride reacts with hydrochloric acid to form ammonium chloride and chlorine, so these halogen derivatives, if

analogous to the nitrogen trichloride, ought to react similarly, forming the corresponding amide. And the fact that they do act thus is a strong argument, therefore, in favor of the view that these derivatives are like nitrogen trichloride and hence substitution-products. A comparison of these two equations brings out this analogy:

(1) $NCl_3 + 3HCl = 6Cl + NH_3 + HCl(NH_4Cl)$.

(2) $C_6H_5SO_2N.Cl_2 + 2HCl = 4Cl + C_6H_5SO_2NH_2$.

3. The halogen derivatives of the sulphonamides are good oxidizing agents; and whenever they act thus it is with the production of the corresponding sulphonamide as one of the products of the reaction. Such being the case, a determination of the oxidizing power of these derivatives will also show whether they are addition- or substitution-products. If addition-products, such as $C_6H_5SO_2NH_2Cl_2$, they will have an oxidizing power equivalent to one atom of oxygen, thus:

I. $C_6H_5SO_2NH_2Cl_2 + H_2O = C_6H_5SO_2NH_2 + 2HCl + O$.

Whereas, if these halogen derivatives be really substitution-products, then each molecule of the compound will have an oxidizing power equivalent to 2 atoms of oxygen, thus:

II. $C_6H_5SO_2N.Cl_2 + 2H_2O = C_6H_5SO_2NH_2 + 2HCl + 2O$.

This point has been thoroughly tested with such reducing agents as sulphurous acid, hydriodic acid, and sodium arsenite with the following results:

With Sulphurous Acid.

1 cc. H_2SO_3 solution is equivalent to 2.4 cc. 1/10 normal iodine solution.

Experiment 1.— Took 0.1996 gram benzenedichlorsulphonamide with 20 cc. sulphurous acid solution. After standing until the chlorine compound was dissolved the solution required 16 cc. 1/10 normal iodine solution to complete the oxidation of the H_2SO_3. Hence the sulphurous acid oxidized by chlorine compound = 0.1312 grams. Calculated according to equation II, 0.1449 grams.

Experiment 2.—Took 0.4639 gram of benzenedibromsulphonamide with 40 cc. sulphurous acid solution. After solution of the bromine compound the solution took 40 cc. 1/10

normal iodine solution. Hence the sulphurous acid oxidized by bromine compound = 0.2296 gram. Calculated = 0.2415 gram.

Experiment 3.—In experiments 3 and 4, 1 cc. H_2SO_3 used = 1.28 iodine solution; 1 cc. iodine solution = 0.0128 gram iodine. Took 0.1704 gram bromine compound with 50 cc. sulphurous acid. Allowed to stand several hours. It took 42 cc. iodine solution to complete oxidation. Hence the sulphurous acid oxidized by bromine compound = 0.091882 grams; calculated = 0.088716 grams.

Experiment 4.—Dissolved 0.1788 gram of (*p*)-toluenedichlorsulphonamide, $C_6H_4<\begin{matrix}SO_2N.Cl_2\\CH_3\end{matrix}$, in potassium iodide solution. To this solution added 50 cc. sulphurous acid. Titrated with iodine solution. It took 33.1 cc. iodine solution. Hence the sulphurous acid oxidized by this chlorine compound = 0.1276 grams; calculated 0.1221 grams.

With Dilute Hydriodic Acid.

Experiment 1.—Took 0.1855 grams benzenedibromsulphonamide in 50 cc. dilute hydriodic acid. Boiled for a few minutes under an inverted condenser; cooled and added 30 cc. hyposulphite 1/10 normal, and titrated with 1/10 normal iodine solution. It took 6.2 cc. iodine solution. Hence a quantity of iodine was liberated from the hydriodic acid by the bromine compound, equivalent to 23.8 cc. $Na_2S_2O_3$ 1/10 N = 0.3024 gram I; calculated according to equation = 0.3006 gram I.

$$C_6H_4SO_2N.Br_2 + 4HI = C_6H_5SO_2NH_2 + 2HBr + 4I.$$

Experiment 2.—Took 0.1612 gram benzenedichlorsulphonamide with 50 cc. dilute hydriodic acid. Treated as in the preceding experiment. Added 30 cc. $Na_2S_2O_3$ 1/10 normal, and titrated with iodine solution. Took 2.4 cc. normal iodine solution. Hence a quantity of iodine was liberated from the hydriodic acid by the chlorine compound equivalent to 27.6 cc. $Na_2S_2O_3$ 1/10 N; Hence, found = 0.3515 gram I; calculated as above = 0.3623 gram I.

With Arsenious Acid. (*Sodium Arsenite 1/10 N.*)

Experiment 1.—Boiled 0.1676 gram of benzenedibromsul-

phonamide with 30 cc. arsenite solution. Cooled and titrated with 1/10 normal iodine solution. Took 7.6 cc. iodine solution. Hence there was formed As_2O_5 equivalent to 22.4 cc. arsenite solution 1/10 normal = 0.1287 gram As_2O_5; calculated according to equation below = 0.1223 gram As_2O_5.

$$C_6H_5SO_2N.Br_2 + 2H_2O + As_2O_3 = C_6H_5SO_2NH_2 + 2HBr + As_2O_5.$$

Experiment 2.—Took 0.1172 gram benzenesulphonamide with 50 cc. As_2O_3 solution 1/10 normal. Boiled, cooled, and titrated with iodine solution, 1 cc. of which contains 0.0128 gram I. Took 14.7 cc. iodine solution. Hence a quantity of As_2O_5 was formed by the bromine compound equivalent to 14.7 cc. of the iodine solution; found = 0.0852 gram As_2O_5; calculated according to equation above = 0.0855 gram As_2O_5.

Experiment 3.—Took 0.1834 gram of *p*-toluenedichlorsulphonamide, $C_6H_4<^{CH_3}_{SO_2N.Cl_2(p)}$. Boiled with 40 cc. 1/10 normal As_2O_3 solution. This took 9.3 cc. iodine solution used in experiment 2. Hence a quantity of As_2O_5 formed by the chlorine compound, equivalent to 29.9 cc. of this iodine solution. Hence, found = 0.1732 gram As_2O_5; calculated 0.1764 gram As_2O_5.

Experiment 4.—Took 0.2052 gram of *p*-brombenzenedichlorsulphonamide, $C_6H_4<^{SO_2N.Cl_2}_{Br(p)}$, with 40 cc. 1/10 normal As_2O_3. Boiled, cooled, and titrated with same iodine solution as used in experiments 2 and 3 above. Took 12.8 cc. iodine solution. Hence, As_2O_5 found = 0.1530 gram; calculated = 0.1547 gram.

In the light of these results it is readily seen that these compounds have an oxidizing power equivalent to two atoms of oxygen, and that hence they are to be regarded as *substitution*-rather than *addition*-products of the sulphonamides. In view of these results it is proposed to call these two classes of derivatives, dichlorsulphonamides and dibromsulphonamides, respectively. This nomenclature has been employed, we believe, correctly, throughout this paper, using with the name dichlor- or dibromsulphonamide such prefixes as were

naturally suggested by the composition of the compounds. While the results above described seem to leave no doubt as to the nature of these derivatives, other methods of proof have already suggested themselves which will be tested in due time, and several interesting syntheses seem possible through the use of these derivatives, which we soon hope to attempt.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, April, 1896.

THE REDUCTION OF COPPER SULPHIDE.

BY DELIA STICKNEY.

J. Uhl in his paper[1] "Ueber Einwirkung von Schwefeldioxyd auf Metalle" speaks of reducing copper sulphide by heating it in a stream of hydrogen. A simpler way to accomplish the reduction is to let the compound come in contact with the flame of the ordinary Bunsen burner until a change in color is seen. Copper sulphide made by heating copper turnings and flowers of sulphur in an ignition-tube was held by forceps in the flame for five or ten minutes. The bluish-black sulphide turned dark red, and the odor of sulphur dioxide was noticed. To determine whether this was metallic copper or cuprous oxide, the experiment was made on a larger scale. Copper sulphide prepared in the usual way was ground, and heated in a porcelain dish with the flame playing directly upon it. During the heating, the mass showed blue, green, and black colors, shades of red and of metallic copper, and under the lens, many threads of bright copper were distinctly seen in the soft, spongy mass. The unreduced part was hard and brittle, but the colored parts were soft and friable. After successive grindings and heatings, very few hard lumps remained, but each time the mass felt softer under the pestle, and looked more like spongy copper.

To see if cuprous oxide was formed in any great amount, equal quantities of this product and of cuprous oxide were treated with concentrated hydrochloric acid, cuprous oxide dissolved entirely, but the other left a bright residue in the bottom of the tube. A test with ammonia showed that but little had dissolved. The residue was taken out, dried upon

[1] Ber. d. chem. Ges., **23**, 1215.

filter paper, and examined under a lens. The greater part was bright copper but there were also some particles of a dark color, probably a little of the sulphide not reduced. Some of the product obtained by grinding and heating in this way was put into the flame of the blast lamp, and heated gradually until the copper melted. A little matte, tarnished on the outside, was formed in the bottom of the dish, which analysis showed to contain 97—98 per cent. pure copper.

Experiments were now made with copper sulphide heated under different conditions. It was used just as it came from the tube, and heated undisturbed for one to four hours. The hard, black mass gradually fell apart loosely, and formed the most beautiful product that had been obtained. Varying shades of red were seen, mixed with iridescent, bluish-black parts, arranged often in bands, and in the centre, and on the bottom, the little bright sheafs of metallic copper containing threads one-fourth to one-half inch in length were very abundant. To see if greater heat hastened the process, the sulphide was heated in the same way by the blast lamp. It melted a little on the edges, but remained a hard, brittle, gray mass with but little of the red color on it, showing that the gentle reducing action of the Bunsen flame was needed rather than a high degree of heat.

Once the sulphide came from the tube in which it was made, so hot that the free sulphur burned in the air. When the action was over, a few red spots were seen here and there. This suggested that a little free sulphur might hasten the reduction, and when the process was half completed, the addition of this seemed to shorten the time. Cupric oxide and cuprous oxide were intimately mixed with sulphur and heated, and here the reduction to copper was much quicker than in the case of the sulphide.

For the purpose of determining if contact with the flame was essential, some of the sulphide was heated for four to five hours in a porcelain crucible with the flame underneath, free contact with the air being allowed. Hardly any change in color was seen. On the top there was a slight reddish tinge, and a little sulphur was set free, but the mass was still hard and dark, keeping its shape. The form of the sulphide seemed to make

no difference, for the results were the same whether it was powdered or in the form of filings or foil.

This easy method of reduction may be of use in general chemistry, as forming the complementary part of the familiar experiment with copper and sulphur, illustrating synthesis. The pupils' questions show always the desire to reverse the process, and get the copper back again.

ENGLISH HIGH SCHOOL, CAMBRIDGE, MASS.
April, 1896.

REVIEWS AND REPORTS.

A YEAR'S PROGRESS IN THE FIELD OF CARBOHYDRATES.

During the year 1895 the activity devoted to research among the carbohydrates has in no wise abated, and although no results of a striking character have been obtained as compared with those of some recent years, there has been evident progress toward a more definite and scientific knowledge of these bodies. In the following lines an attempt is made to bring together the gist of most of the papers published during this time, although in so broad a field it will not be surprising if a few publications have been overlooked. No attempt has been made to include in this review the strictly technical publications.

General Reactions.

The most important general reactions of sugars brought out during the year is the so-called glucoside synthesis discovered by Fischer and his pupils. Although the reaction was noted in development in 1894, its perfected form has been announced during the last year. Ether-like compounds between the sugars and a considerable number of alcohols are made by mixing the constituents and subjecting them to the action of a very small amount of hydrochloric acid. From the resulting solutions the new glucosides crystallize freely upon concentration.[1] In this way compounds between most of the glucoses or mono-saccharides and methyl and ethyl alcohols and acetone[2] have been prepared. These bodies are of the nature of ethers and are very suggestive of the natural glucosides. It is thought that this use of small amounts of acids to bring about similar reactions will prove of general application.

Another reaction of a general nature is that occurring be-

[1] E. Fischer: Ber. d. chem. Ges., **28**, 1145, 1167; also A. Speier: *Ibid.*, **28**, 2531.
[2] C. Councler: *Ibid.*, **28**, 24.

tween the glucoses and ammonia.[1] The sugars are found to be appreciably soluble in absolute methyl or ethyl alcohols in the presence of ammonia, from which solution there separates on standing a crystalline compound of imide character. The compounds are fairly stable, although, after some time, ammonia is slowly set free. The structure is supposed to be that represented by the formula

$$CH_2OH.(CHOH)_3.\overset{NH}{\overset{/\quad\backslash}{CH}}-CHOH.$$

Such compounds of ammonia with dextrose, lactose, maltose, galactose, xylose, arabinose, rhamnose, fructose and mannose, have been prepared, for which the discoverers proposed the name "osamines."

Certain sugars (dextrose, levulose and mannose) exhibit a change in their specific rotation when in contact with dilute solutions of the alkalies or alkaline earths. This has been overlooked in the many studies of the action of alkalies on sugars. It now appears that this is due to intramolecular changes by which either of these three sugars may respectively be transformed into the other.[2] This occurs most easily with a small amount of the alkali (about one per cent.). The authors explain the reaction as follows: R.CHOH.CHO becomes $R.\overset{O}{\overset{/\quad\backslash}{CH}}-CHOH$, or $R.CO.CH_2OH$. The possibility of such changes as these may throw light upon the phenomenon of multirotation and upon many other reactions. They are particularly suggestive in connection with Fischer's syntheses, where the reduction of certain acids in alkaline solution led to aldoses or alcohols of a different series.

The possibility of the existence of isomeric acetyl derivatives of the same sugar according to whether sodium acetate or zinc chloride is used in their preparation has been studied.[3] The stable compounds like inosite yield the same product with either reagent. With sodium acetate the di-saccharides yield products which permit the regeneration of the sugar, but not with zinc chloride. The glucoses yield three different bodies if treated with one or the other of these reagents or a mixture of the two.

The actual synthesis of new sugars has naturally not received many contributions. Fischer[4] has given a very inter-

[1] C. A. Lobry de Bruyn: Ber. d. chem. Ges., **28**, 3082; also Recueil des Travaux des Pays-Bas., **14**, 98 and 135; W. E. Stone: This JOURNAL, **17**, 196.

[2] C. A. Lobry de Bruyn and W. van Ekenstein: Ber. d. chem. Ges., **28**, 3078.

[3] C. Tanret: Compt. Rend., **120**, 194. [4] Ber. d. chem. Ges., **27**, 3189.

esting review of his work in which he states that no observation in this field conflicts with the theory of the asymmetric carbon atom, and in which he points out that configuration has a marked influence upon the physical, chemical and physiological properties of sugars. In continuation of his synthetical studies,[1] the *d*- and *l*-gulonic acids obtained respectively from *d*-gluconic and xylose-carbonic acids have been transformed by heating with pyridine into *d*-idonic and *l*-idonic acids, and these by reduction into the *d*- and *l*-idoses respectively, and finally into *d*- and *l*-idite, the latter being quite different from mannite. On combining the two active bodies in each case there were obtained the inactive idonic acid, idose and idite. These compounds complete the possible members of the mannite series.

New Carbohydrates.

The subtance volemite, mentioned by Bourquelot as being obtained from the fungus *Lactarius volemus* is identified by Fischer as a heptavalent alcohol or heptite, $C_7H_{16}O_7$, which by mild oxidation is converted into heptose.[2] This differs from the synthetic gluco- and gala-heptites and constitutes the second known natural heptite.

A substance has been obtained from young rye plants which is soluble in water with a specific rotation of $(\alpha)_D = 28°.9$, and easily converted into levulose. The name of *β*-levulose, or preferably secalose, has been assigned to it.[3]

The sugar agavose, from the *Agave Americana*, has been shown to be sucrose.[4]

By acting on amygdalin with the yeast enzyme which converts maltose into dextrose, it is found that one-half of the theoretical amount of sugar is set free. There remains a new substance, which upon hydrolysis with hydrochloric acid, breaks up into benzaldehyde, prussic acid and a second molecule of dextrose.[5] This would indicate that amygdalin contains a maltose molecule, one-half of which can be split off without affecting the glucoside structure.

Glucoses or Mono-saccharides.

Glycerose is said to be formed on treating glycerin with mercuric chloride. At 160° the reaction becomes violent and calomel is rapidly thrown down. A number of products distil off, among which glycerose was recognized by the reduc-

[1] E. Fisher and I. Fay: Ber. d. chem. Ges., **28**, 1975 and 1981.
[2] E. Fischer: *Ibid.*, **28**, 1973.
[3] Schulze and Frankfurt: *Ibid.*, **27**, 3525.
[4] Stone and Lotz: This JOURNAL, **17**, 368.
[5] E. Fischer: Ber. d. chem. Ges., **28**, 1508.

tion of Fehling's solution in the cold, and by phenylhydrazine compounds; but it was optically inactive.[1]

Pentoses.—Xylose has been prepared from the cocoanut shell by mild hydrolysis, and, on using more concentrated acids, dextrose was also obtained from the same source.[2]

Arabinose is produced by hydrolysis of the gum of *Acacia decurrens*, in connection with galactose—a result quite similar to that obtained from gum arabic.[3]

From xylan, monobenzoyl and monoacetyl esters have been prepared.[4] Tetra-acetyl xylose and the oxidation of xylose to trioxyglutaric acid, mentioned by the same author, have been previously described by other investigators.

Arabinose and xylose compounds of chloral have been prepared, both products yielding a characteristic blue color with orcin hydrochloride.[5]

A compound of arabinose with benzhydrazide has been made similar to that with dextrose, described below.[6] Ether-like compounds of both arabinose and xylose with alcohols, acetone, and also phloroglucin have already been mentioned.

The preparation and properties of crystallized rhamnose are described in connection with its compounds with alcohols and acetone.[7]

The physiological aspects of the pentoses and pentosans still attract attention. Sixty-five per cent. of the pentosans in fodder was digested by sheep and fifty-three per cent. by rabbits. That portion digested did not seem to be assimilated, since pentoses constantly appeared in the urine of the animals.[8] Pentoses are frequently noted in urine and the phenomenon is the excuse for a new term "pentosurie."[9] This occurrence does not accompany diabetes and is not to be regarded as an alarming condition.[10]

Hexoses.—Dextrose combines with alcohols and acetone to a kind of glucoside, as already described. Two acetone derivatives were thus obtained, dextrose-diacetone, which can be sublimed, and a mono-acetone, soluble and non-sublimable. These compounds are not affected by yeasts or yeast enzymes, and are, therefore, probably of different structural character from the glucosides or di-saccharides.[11]

1 Fonces-Diacon: Bull. Soc. chim., Paris, [3], **13**, 862.
2 B. Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 306.
3 W. E. Stone: This JOURNAL, **17**, 196.
4 R. Bader: Chem. Zeit., **19**, 55.
5 M. Hanriot: Compt. Rend., **120**, 21.
6 Radenhausen: Zeit. Ver. Rübenzuck, Ind., 1894, 768.
7 E. Fischer: Ber. d. chem. Ges., **28**, 1162, 1158.
8 H. Weiske: Ztschr. physiolog. Chem., **20**, 489.
9 E. Salkowski: Berl. Klin. Woch, schr., **32**, 364.
10 F. Blumenthal: *Ibid.*, **32**, 567.
11 E. Fischer: Ber. d. chem. Ges., **28**, 2496

By treating the glucoses (mono-saccharides) with benzhydrazide in alcoholic solution, hydrazides are formed, which are soluble in water. On heating them with benzaldehyde they are decomposed with regeneration of the glucose. In this way dextrose can be separated from the levulose of invert sugar, levulose not entering into the reaction.[1] Attempts have also been made to prepare similar derivatives with semicarbazide, but without definite results, although they all behaved like the hydrazides toward benzaldehyde.[2]

Molecular modifications of dextrose have been noted, each of different rotatory power, and formed under different conditions of crystallization. α-glucose ($(\alpha)_D = 106°$), β-glucose ($(\alpha)_D = 52°.5$), and γ-glucose ($(\alpha)_D = 22°.5$), are described. These have the same molecular weights but different heats of solution. Similar modifications of other sugars could not be prepared.[3]

The transformation of dextrose into mannose or levulose as well as the preparation of dextrosamine with ammonia have already been mentioned.

Dextrose has been obtained by the hydrolysis of cocoanut shells,[4] and from the sumach (*Rhus*).[5] The sugar obtained from indican, either by hydrolysis or ferments is dextrose.[6]

The inversion of starch for the production of crystallized dextrose is advantageously preformed by heating with dilute oxalic acid, eventually under pressure.[7]

Levulose, generally regarded as an unstable sugar, is found to undergo deep-seated changes when heated with water from 100° to 120°. Humus-like substances are formed and a mixture of furfurol, formic acid and formaldehyde distils over.[8]

By the action of oxalic acid on levulose under pressure, β-oxy-γ-methylfurfurol was formed. Sorbinose seems to undergo a similar change, which would indicate a tendency of the ketose sugars to form cyclic compounds,[9] The aldoses undergo no such change.

Levulose has been prepared from orange peel.[10] It shares in the general reactions already referred to under the glucoside syntheses, and the transformation into dextrose and mannose.

[1] H. Wolff: Ber. d. chem. Ges., **28**, 160; also Th. Curtius: *Ibid.*, 522.
[2] A. and W. Herzfeld: Zeit. Ver. Rübenzuck. Ind., 1895, 853.
[3] C. Tanret: Compt. Rend., **120**, 1060.
[4] Tollens and Tromp de Haas; Ann. Chem. (Liebig), **286**, 386.
[5] C. Böttinger: Archiv. f. Pharm., **233**, 125.
[6] C. J. van Bookeren: Landw. Versuch. Stat., **45**, 195.
[7] C. J. Lintner and G. Düll: Ber. d. chem. Ges., **28**, 1522.
[8] B. Rayman and O. Sulc: Böem. Zeit. f. Zuck. Ind., **19**, 765.
[9] J. Keiermayer: Chem. Zeit., **19**, 1003.
[10] R. W. Bauer: Landw. Versuch. Stat., **45**, 293.

Mannose can be prepared from vegetable ivory by hydrolyzing with hydrochloric acid and precipitating the mannose as a hydrazide, which, on treatment with benzaldehyde suffers decomposition, the mannose being liberated in pure form.[1] The transformation of the mannose into dextrose aud levulose as well as its share in the glucoside reactions has been noticed.

Galactose has been obtained from the gum of *Acacia decurrens*, which probably contains a galacto-araban complex capable of hydrolysis.[2] Compounds of galactose with alcohols and phloroglucin have been noted.

Disaccharides.

Sucrose.—As the result of rather extended observations by himself and his pupils, Schulze regards sucrose as a form of reserve food in the plant, derived probably from starch of which it is a transport form.[3] Of interest are the recorded occurrences of sucrose in seeds and plants from which it has been separated by the strontian method. Among seeds containing sucrose, are noted oats, rye, wheat, buckwheat, ripe and unripe peas, soja bean, peanut, hemp, sunflower, coffee, and lupine; sucrose is found in etiolated germinating plants of lupine, sunflower, vetch, and potato; in green plants of rye, vetch, potato, elder and hazel; in tubers of potato and roots of the carrot and in the flowering buds of the pear.

From a careful study of the action of acids upon sucrose for purposes of inversion it appears that acetic acid produces complete inversion, but that the optical properties of such a product are different from those of a solution inverted by hydrochloric acid.[4]

It has been claimed that citric acid is produced when sucrose is oxidized by potassium permanganate, but this has been vigorously denied by several experimenters who at least have been unable to obtain the results described.[5]

Sucrose combines with litharge to form a compound with the formula $C_{12}H_{18}O_{11}Pb_25H_2O$. This is readily precipitated when litharge is mixed to the consistency of a paste, with molasses. The compound can afterwards be decomposed with carbon dioxide, leaving a pure sugar solution. The method is adapted to the recovery of sugar from molasses.[6]

Lactose.—Molecular modifications of lactose have been announced similar to those of dextrose.[7]

[1] Duyvene de Witt, Zeit. Ver. Rübenzuck. Ind., 1895, 794.
[2] W. E. Stone, This JOURNAL, **17**, 196.
[3] E. Schulze and S. Frankfurt, Ztschr. physiolog. Chem., **20**, 511.
[4] H. A. Weber and W. McPherson, J. Am. Chem. Soc., **17**, 368.
[5] T. Phipson, Chem. News, **71**, 296; also **72**, 31, 100, 165, 190, 235, 268.
[6] G. Cassner, Dingl. Pol. Jour, **298**, 65.
[7] Compt. Rend., **120**, 1060.

one with the specific rotation of $(\alpha)_D = 55°$ and the other 34°.[1]

Maltose.—The oct-acetyl derivative of maltose has been subjected to repeated study, and its properties described somewhat differently from those given in the original paper by Herzfeld.[2] [3]

Maltose can be regenerated from its hydrazide by the substituting action of benzaldehyde.[4] By the action of fuming hydrochloric acid on dextrose, maltose is said to be formed and by longer action dextrins result. This reaction reminds one of the glucoside synthesis, and it is probable that the synthesis of the complex sugars will eventually be accomplished along this line.[5]

Raffinose has been noted in the germs of wheat, thus adding one more to the rather unusual occurrences of this sugar.[6]

Of the polyvalent alcohols, mannite seems to be of common occurrence in nature, as is also dulcite. The Schrophulariaceæ are particularly productive of these bodies.[7] Mannite forms a tri-acetone compound.[8]

Amorphous Carbohydrates.

An amorphous substance extracted from *Polyporous betulinus* has been named paraisodextran. Its formula is $C_6H_{10}O_5$, and by hydrolysis it yields dextrose.[9]

The pectins are regarded by Tollens as being closely related to the carbohydrates as chiefly indicated by their hydrolytic products. It is pointed out that they are of an acid character, as shown by their solubility in alkalies. It is probable that they contain the carboxyl group, COOH, and that they are oxy-derivatives of the mucous bodies.[10]

Cellulose.—The researches of Cross, Bevan, and their associates, upon cellulose, are among the most interesting of those of recent date on the carbohydrates, especially in view of their technical application.[11]

The general results of these investigations go to show that cellulose, in the general sense, or the fibers of plants are not at all of homogeneous character. The different constituents of cellulose are distinguished by their resistence to or be-

[1] Tanret: Bull. Soc. Chim., Paris, [3], **13**, 625.
[2] A. Ling and J. Baker: Chem. News, **71**, 71; and Ber. d. chem. Ges., **28**, 440.
[3] A. Herzfeld: Ber. d. chem. Ges., **13**, 267.
[4] A. Herzfeld: *Ibid.*, **28**, 440.
[5] H. Ost: Chem. Zeit., **19**, 1501.
[6] E. Schulze and S. Frankfurt: Ztschr. physiolog. Chem., **20**, 511.
[7] Monteverde: Annales Agronom., **19**, 444.
[8] E. Fischer: Ber. d. chem. Ges., **28**, 1168.
[9] E. Winterstein: *Ibid.*, **28**, 774.
[10] Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 278.
[11] Cellulose: by Cross and Bevan: (Longmans, Green & Co., 1895.)

havior toward certain reagents. Typical cellulose is a polyhydroxylated body, forming a variety of compounds with acids and alkalies, such as alkali-cellulose-xanthate, acetyl, benzoyl and nitrated compounds.

Compound celluloses or ligno-celluloses, found in most plant fibers, are regarded as more or less oxidized derivatives of pure cellulose. These latter are unstable and tend to form cyclic compounds, such as furfurol, lignone, and keto-R-hexene bodies.

Significant among these secondary celluloses are certain bodies which, upon distillation with acids, yield furfurol in considerable quantities. These the authors regard as being distinct from the pentosans, of which bodies this reaction was heretofore supposed to be characteristic. Tollens confirms this view, but points out that these furfurol-yielding bodies (or furfuroids as Cross suggests) are nevertheless of very indefinite and, so far, little understood substances.[1] E. Schulze, whose work in this field entitles his opinion to much respect, intimates that it is still much too early to attempt any definite classification of the forms and varieties of cellulose.[2]

Cellulose is at least of quite a different chemical character from starch, as shown by its greater resistance to hydrolysis. In many respects it behaves like a salt, forming, for instance, with zinc salts, double salt-like compounds, and it acts as an electrolyte to the extent that, when subjected to an electric current, metals are transferred from the anode to the cellulose fiber. Pure cellulose can apparently be transformed to some extent into oxy-cellulose under the action of concentrated sulphuric acid.[3]

Pure anhydrous cellulose shows a distinct rise of temperature when placed in a moist atmosphere, indicating the formation of a definite compound.[4]

By the action of nitric acid on ligno-cellulose, energetic oxidation takes place and reduced oxides of nitrogen are liberated. Unchanged fiber, volatile acids, oxalic acid and soluble derivatives result. The reaction consists in the main of the destructive oxidation of the non-cellulose groups.[5]

Cellulose-di-sulphuric acid results from the solution of cellulose in concentrated sulphuric acid.[6]

[1] Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 296.
[2] E. Schulze: Chem. Zeit., **19**, 1465.
[3] Cross, Bevan and Beadle: Chem. News, **71**, 121.
[4] Clayton Beadle: *Ibid.*, **71**, 1.
[5] E. Baley and J. Chorley: *Ibid.*, **71**, 226.
[6] A. L. Stern: *Ibid.*, **70**, 267.

Cellulose from certain fungi, particularly *Boletus edulis*, when heated with strong hydrochloric acid, yields glucosamine chloride, which would indicate a substance resembling chitin in this material.[1]

In the cell walls of yeast there are thought to be two kinds of cellulose, one stained by iodine and soluble in water, and the other not stained and insoluble. The latter yields some mannose in addition to dextrose when hydrolysed.[2]

Starch.—Discussion goes on unremittingly as to the nature of the many products resulting from the action of acids or ferments upon starch. Different English and German chemists strongly doubt the existence of the so-called isomaltose,[3] while Lintner and E. Fischer still maintain its individuality.[4] The former even distinguishes two forms of isomaltose, differing in their susceptibility to diastatic action and in fermentability by certain yeasts.[5] Brown and Morris point out that the products of the action of diastase on starch behave like a mixture of maltose and dextrin as regards their rotation and reducing power. Apparent exceptions where the action has taken place in the cold, are due to the semi-rotation of maltose under such conditions.[6]

An attempt to determine the molecular weights of the soluble forms of starch by analysis of their baryta compounds, while not leading to exact results, showed that amylo-dextrin, erythro-dextrin and achroo-dextrin possess diminishing molecular weights in the order named.[7]

A study of the comparative action of oxalic acid and diastase upon starch shows that the products are similar, except that maltose is not found as a result of the acid treatment.[8]

Starch is converted into sugar by saliva, pancreas extract and by the blood.[9]

The amount of iodine fixed by potato starch differs with the conditions. The maximum is 18.6 per cent. in the presence of an excess of the reagent; the iodine thus combined reacts with sodium thiosulphite.[10]

1 E. Winterstein: Ber. d. chem. Ges., **28**, 167; also E. Gilson, *Ibid.*, 821.

2 E. Salkowski: *Ibid.*, **27**, 3325.

3 Ling and Baker: Chem. News, **71**, 71; and **72**, 45; also Brown and Morris: *Ibid.*, **71**, 125, and **72**, 45; H. Mittelmeier: Wchschr. Brau., **12**, 480; H. Ost: Chem. Zeit., **19**, 1501.

4 E. Fischer: Ber. d. chem. Ges., **28**, 3024.

5 C. J. Lintner: Zeit. gesamt. Brauw., **17**, 378, and **18**, 173.

6 Chem. News, **71**, 123.

7 K. Bülow: Pflüger's Archiv., **62**, 131.

8 C. Lintner and G. Düll: Ber. d. chem. Ges., **28**, 1522.

9 C. Hamburger: Dissertation, Physiol. Inst., Breslau, 1895.

10 Gaston Rouvier: Compt. Rend., **120**, 1179.

Analytical.

In the determination of sucrose by inversion, the invert sugar is said to have only 96 per cent. of the reducing power of dextrose. O'Sullivan finds that, if very dilute acid be used in the cold for inversion, the product has from 98.7 to 100.8 per cent. of the reducing power of dextrose, and that practically the same factor may be used.[1]

A method is proposed for the estimation in the same material of sucrose, maltose, dextrose and dextrin by the use of a formula employing density, rotation, and reducing data.[2]

The reducing power of maltose is found to vary according to whether sodium or potassium hydroxide is employed in the Fehling's solution. Dextrose shows no such variation.[3]

In the presence of neutral or basic lead acetate the Fehling's test gives less sugar than otherwise, while the presence of salts giving an alkaline reaction with litmus increases the reduction.[4]

Some time since an alkaline solution of potassium copper sulphate was suggested as a substitute for the ordinary Fehling's solution, and now some modifications are proposed to this in the way of greater dilution which promises to give better results.[5]

If the Fehling's test be made with the surface of the liquid fully exposed to the air, more or less of the sugar becomes oxidized by the alkali and the apparent amount of sugar is diminished. This objection may be overcome by covering the liquid with oil or boiling in flasks.[6]

A new method for determining the amount of cuprous oxide thrown down in the Fehling's test is to dissolve the precipitate in nitric acid, add an excess of potassium iodide and titrate the solution with standardized sodium thiosulphate.[7]

For the determination of starch, various modifications of the use of malt extract are suggested also by comparison of color produced by iodine with the color obtained from a standard solution.[8]

Action of Ferments and Enzymes.

Increased attention has been given to the action of yeasts

[1] J. O'Sullivan: J. Soc. Chim. Ind., **14**, 555.
[2] Weber and McPherson: J. Am. Chem. Soc., **17**, 312.
[3] T. A. Glendenning: Chem. News, **72**, 254.
[4] A. Borntrager: Stazione speriment. agric. Ital., **28**, 449.
[5] H. Ost: Chem. Zeit., **19**, 1784.
[6] J. Kjeldahl: Chem. Zeit., **19**, 218.
[7] E. Riegler: Wein. Med. Blatt, **22**, 344.
[8] P. Hibbard: J. Am. Chem. Soc., **17**, 64; M. Dermstedt and F. Voigtländer: Hamburg Staats Chem. lab. J. Krieger: Amerik. Bierbrauer, **27**, 580.

and enzymes upon sugars. It appears that many of these agents act selectively, inverting certain sugars and not affecting others.[1] Ordinary beer yeast yields a soluble substance, which inverts both sucrose and maltose. A similar extract from the "kefir" yeast inverts lactose. An extract from *Schizo-saccharomyces octosporus* completely inverts maltose, but is without effect on sucrose. From *S. maximus* was obtained an enzyme with exactly the opposite property of inverting sucrose, and not maltose. These enzymes receive the names of invertin and maltase. *Monilia candida* contains maltase, but no invertin. It is well known that different species of yeast are of quite different fermenting powers, and this is doubtless due to their specific enzymes.

Melibiose, resulting from the partial decomposition of raffinose, is not affected by invertin from ordinary yeast.[2] This is proposed as a means of estimating raffinose, solutions containing the same to be inverted by invertin, leaving the melibiose unchanged.[3] Maltose behaves differently towards the invertin or glycase of yeast and the glycase of grains.[4]

Fischer shows in an interesting way that the action of enzymes on sugars is modified by the configuration of the latter.[5] For instance, only those glucosides which contain the dextrose molecule are susceptible to the yeast enzyme. Emulsin, however, acts upon glucosides containing either the dextrose or galactose molecule. Only the so-called β-galactosides were so decomposed and, since lactose shows the same relation, it is regarded as having a similar constitution. The methyl derivatives of gluco-heptose, rhamnose, arabinose and xylose are not so affected, and it is noticeable that they all belong to the "*d*-dextrose" series. These data will also throw light upon the constitution of the di-saccharides. For the three best known of this group, sucrose, lactose and maltose, exist specific enzymes, invertin, maltase and lactase. The behavior of the less definitely studied di-saccharides toward these enzymes will establish their relationship to one or the other of those whose structure is to some extent known.

W. E. Stone.

April 15, 1896.

[1] E. Fischer and P. Lindner: Ber. d. chem. Ges., **28**, 984.
[2] *Ibid.*, 3034.
[3] A. Bau: Chem. Zeit., **18**, 1794.
[4] C. Lintner and E. Kröber: Ber. d. chem. Ges., **28**, 1050.
[5] *Ibid.*, **28**, 1429.

A PHYSICAL-CHEMICAL STUDY OF THE GAS BATTERY.

The van't Hoff theory of osmotic pressure and the Arrhenius theory of the dissociation of electrolytes have led in the hands of Nernst[1] to a more or less satisfactory expression for the electromotive force of concentration elements, liquid elements, etc. This has been developed very clearly by Ostwald in his Lehrbuch[2] which, together with the original paper by Nernst, must be consulted for details.

The theory of the gas battery being but an extension of the theory of the liquid element furnishes another means of testing experimentally these well known and very important developments.

Take a simple example of the gas battery, hydrogen over one electrode, and chlorine over the other, using platinum electrodes, and hydrochloric acid as the electrolyte. Hydrogen and chlorine will pass into solution at the two poles until there is an equilibrium between the force driving these substances into solution and the osmotic pressure of the hydrochloric acid solution which acts against the above-mentioned force. The hydrogen pole is negative, since the solution-tension of the hydrogen is greater than the osmotic pressure of the solution, the hydrogen atoms becoming ions by taking positive electricity from the platinum electrode, which thus becomes negative. Exactly the reverse takes place at the other electrode, chlorine atoms becoming ions by taking negative electricity from the electrode, which therefore becomes positive.

The electromotive force, in terms of the Nernst theory, is deduced thus by Smale:[3]

Let P_1 be the solution-tension of hydrogen.
" P_2 " " " " " chlorine.
" T " " " absolute temperature.
" p_1 and p_2 be the osmotic pressures of the electrolytes used, and π_1 and π_2 the E. M. F. at the hydrogen and chlorine poles, respectively.

The electromotive force at the hydrogen electrode is expressed thus:

$$\pi_1 = 0.0002\ T \log. \frac{P_1}{p_1} \text{ volts.}$$

But since the solution-tension of chlorine, oxygen, etc., is negative, the electromotive force at this pole is,

$$\pi_2 = 0.0002\ T \log. \frac{p_2}{P_2} \text{ volts.}$$

[1] Ztschr. phys. Chem., **4**, 129. [2] Lehrb. Bd., **2**, 825–845.
[3] Ztschr. phys. Chem., **16**, 562.

The electromotive force of such a system would be,

$$\pi_1 - \pi_2 = \pi_0 = 0.0002\ T \log. \left(\frac{P_1}{p_1} - \frac{p_2}{P_2}\right).$$

$$= 0.0002\ T \log. \left(\frac{P_1}{p_1} + \frac{P_2}{p_2}\right).$$

The theoretical consequences of this equation are very interesting. P_1 and P_2, the solution-tensions, are independent of the nature and concentration of the electrolyte. p_1 and p_2, the osmotic pressures, change with the concentrations, but for approximately equally dissociated solutions, are practically constant. Smale has shown[1] then, that in terms of the theory, the electromotive force of a hydrogen-oxygen battery should be *independent* of the *nature* and *concentration* of the electrolyte, provided the electrolytes are equally dissociated. For a hydrogen-chlorine battery, the electromotive force *depends on the concentration of the electrolyte*, and increases with increase in dilution.

These points can all be tested rigidly by experiment, and this has been done by Smale,[2] working in the laboratory of Ostwald. The apparatus which he employed is shown in Figs. 1 and 2.

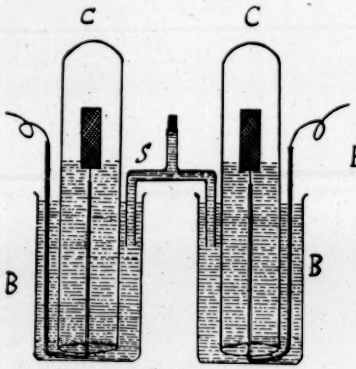


Fig. 1.

Fig. 2.

C C are two glass cylinders dipping into beakers *B B*, which contain a solution of the electrolyte used. The beakers

[1] Ztschr. phys. Chem., **16**, 563. [2] *Ibid.*, **14**, 577.

are connected by the tube *S*, also filled with the electrolyte. The electrode *E*, say of platinum, consists of a strip of this metal, attached to a platinum wire, which is fused into the glass tube, as shown in Fig. 2. Electrical connection with the exterior is made by means of a copper wire, introduced into the glass tube, as shown in Fig. 2. The cylinders are at first filled with a solution of the electrolyte, and the gases introduced by displacement, until the electrode is partly surrounded by the gas and partly by the electrolyte. Strips of platinum, such as are cut from ordinary foil, could not be used directly, since such would not give constant results. It was necessary to cover these with a layer of platinum black, deposited electrolytically upon them, from a dilute solution of platinum chloride.

The electromotive force of a given combination was measured by balancing the battery in question against a Leclanché element, on a specially constructed resistance box, using a Lippmann capillary electrometer, which permitted measurements to 0.0001 volt. The Leclanché element was frequently calibrated by means of a one-volt element, indeed, before and after each measurement. The volt element was compared with a standard Clark element.

The first point tested is whether the electromotive force is independent of the nature and concentration of the electrolyte used, when hydrogen was employed at the one pole and oxygen at the other. The electrolytes comprised seven acids, three bases and seven salts. The concentrations for the same electrolyte vary in most cases from 0.1 to 0.001 normal. The electromotive force of the cell as a whole was measured, and also the tension at each pole, by means of a calomel electrode.[1]

A few results for acid, base and salt are given:

Electrolyte.	Concentration. Normal.	E. M. F. Direct measurement.	Value of the H-Electrode.	Value of the O-Electrode.
Hydrochloric acid	0.1	0.998	0.332	0.665
" "	0.01	1.036	0.391	0.642
" "	0.001	1.055	0.438	0.616
Potassium hydroxide	0.1	1.098	1.027	0.072
" "	0.01	1.095	0.991	0.103
" "	0.001	1.093	0.954	0.137
Sodium sulphate	0.1	1.074	0.547	0.527
" "	0.01	1.069	9.563	0.506
" "	0.001	1.069	0.572	0.497

[1] Ostwald: Hand und Hilfsbuch zur Ausführung physiko-chemischer Messungen, S. 257.

The results substantiate very strikingly the deductions from the theory. Certain discrepancies, however, manifest themselves, but these seem to admit of a satisfactory explanation through the secondary reactions at the oxygen pole.

The second point, that the electromotive force of a hydrogen-chlorine battery, depends on the *concentration* of the electrolyte, increasing with increase in dilution, was then tested. The following results,

Electrolyte.	Concentration. Normal.	Entire E. M. F.	E. M. F. H-Electrode.	E. M. F. Cl-Electrode.
Hydrochloric acid	1.0	1.360	0.288	1.071
" "	0.1	1.472	0.343	1.129
" "	0.01	1.547	0.403	1.144
" "	0.001	1.621	0.456	1.175

bear out the theory on this point. But the theory admits of still further experimental test.

If the electrodes are of two metals, *e. g.*, platinum and palladium, surrounded by the same gases, which do not attack them, and immersed in the same electrolyte, the electromotive force, at each electrode is, in terms of the theory, formulated thus:

$$\pi_1 = 0.0002\ T \log. \frac{P_1}{p_1} \text{ volt};$$

$$\pi_2 = 0.0002\ T \log. \frac{P_2}{p_2} \text{ volt.}$$

P_1 and P_2 are the solution-tensions of the gas in platinum and palladium, respectively; p_1 and p_2 the osmotic pressures at the electrodes, which are equal in this case, since the same electrolyte is used on both sides. Therefore we have

$$\pi_1 - \pi_2 = 0.0002\ T \log. \frac{P_1}{P_2} \text{ volt.}$$

The metal electrodes play then only this rôle, that they offer a large surface to the gas, facilitating its solution. The *electromotive force* of such an element should therefore be *independent* of the *nature* of the electrode used, since the solution-tension is a constant according to the theory. It should, further, be *independent* of the *size* of the electrode.

The first point was tested by means of the oxygen-hydrogen battery, using sulphuric acid as the electrolyte. The metals employed were platinum, palladium and gold.

Electrode.	Entire E. M. F.	Value of the H-Electrode.	Value of the O-Electrode.
Platinum	0.693	0.277	0.417
Palladium	0.684	0.270	0.412
Gold	0.655	0.258	0.415

Again the agreement of fact with theory is fairly satisfactory.

The same combination as that just employed, was used in determining the effect of the *size* of the electrode on the electromotive force of the cell. Platinum electrodes, 3 cm. long, were used, varying in breadth from a wire 0.2 mm. in diameter, to foil 10 mm. across. These results were obtained:

Breadth of electrode. mm.	Entire E. M. F.	Value of H-Electrode.	Value of O-Electrode.
0.2	0.733	0.323	0.410
2.0	1.017	0.317	0.699
7.0	1.073	0.317	0.745
10.0	1.070	0.317	0.744

The size of the electrode, beyond a certain value, has little or no effect upon the electromotive force. Within this value the decrease in the tension is to be sought for at the oxygen electrode, as is seen above. A certain amount of surface is therefore necessary, that the oxygen electrode should reach its full tension, an amount which is not realized in the first two sizes employed. Beyond this point the theory again finds strong support in the facts.

Another point of considerable interest brought out by this work of Smale deals with the temperature-coëfficient of solution-tension. Nernst,[1] the author of the conception of the solution-tension of metals, in referring to thermo-elements, regarded the solution-tension of mercury electrodes as having a *positive* temperature-coëfficient. Smale has tested this experimentally, by determining the electromotive force of an element with hydrogen over both electrodes, which were of platinum, the gas being kept at different known temperatures on the two sides of the cell. The same electrolyte, 0.01, normal sulphuric acid, was used at both poles. The electromotive force of such an element must depend upon two variables, the change in osmotic pressure and the change in the solution-tension of the hydrogen. The results led to the conclusion that the solution-tension *decreases* with increase in temperature. Other work has shown[2] that the solution-tension of metals, which was originally assumed to be a constant independent of the solution, is directly dependent on the na-

[1] Ztschr. phys. Chem., 4, 172. [2] Jones: Ztschr. phys. Chem., 14, 346.

ture of the solvent. The idea of solution-tension has thus already undergone serious modifications, and will probably be regarded with some suspicion, especially if it leads us to such conclusions, as that this pressure is to be represented in such a case as magnesium, by 10^{44} atmospheres.

Smale has pointed out further, another line, along which a physical-chemical study of the gas battery might be extended. That in which the *same gas*, say hydrogen, is used over the two poles, but under *different pressures*. The tension of the individual electrodes would be expressed in this case by

$$\pi_1 = \frac{0.0002\ T}{2} \log. \frac{P_1}{p_1} \text{ volt.}$$

$$\pi_2 = \frac{0.0002\ T}{2} \log. \frac{P_2}{p_2} \text{ volt.}$$

Since P_1 and P_2, the solution-tension of the gas is constant, and p_1 and p_2 are the pressures of the gas at the two electrodes, we have

$$\pi_1 - \pi_2 = \pi = \frac{0.0002\ T}{2} \log. \frac{p_2}{p_1} \text{ volt.}$$

The constant $0.0002\ T$ in the above equation, is divided by 2, since the hydrogen molecule, which passes over into ions, consists of two atoms. This is closely analogous to the concentration element, where the same gas, under the same pressure on both sides, comes in contact with two different concentrations of the same electrolyte. In this case the electromotive force is expressed by the equation,

$$\pi = 0.0002\ T \log. \frac{p_2}{p_1} \text{ volt,}$$

in which p_2 and p_1 are the osmotic pressures of the two solutions of the electrolyte.

To summarize, the work as a whole furnishes another beautiful experimental confirmation of that theory, which has enabled us to calculate the electromotive force of concentration elements, liquid elements, etc., and, for the first time, has furnished us with a satisfactory explanation of the action in the Voltaic cell, although the cell itself has been known for a century.

HARRY C. JONES.

ELEKTRO-METALLURGIE, DIE GEWINNUNG DER METALLE UNTER VERMITTLUNG DES ELEKTRISCHEN STROMES. VON DR. W. BORSCHERS. Second, enlarged, and revised edition. First and second parts, with 188 cuts. Harold Bruhn, Braunschweig, 1895 and 1896. pp. 393.

The rapid strides which electro-metallurgy has made in the

last few years, and the renewed practical interest in the electrolytic deposition of the metals, have created a demand for a new edition of Dr. Borschers' work. The electro-metallurgist will find in this greatly enlarged edition, a clear account of the processes which he may wish to employ, as far as such are ascertainable up to the present. The first division of the book discusses the methods available for obtaining magnesium, lithium, beryllium, sodium, potassium, calcium, strontium, barium, aluminium, cerium, lanthanum, and didymium. The second part has to do with the electro-metallurgy of copper, silver, gold, zinc, cadmium, mercury, tin, lead, bismuth, antimony, chromium, molybdenum, tungsten, uranium, manganese, iron, nickel, and cobalt, and the platinum metals.

The methods employed in obtaining sodium, aluminium, copper, silver, gold, zinc, and lead are discussed at considerable length. The work is introduced by a chapter on electrolysis, so that the scientific electro-chemist, as well as the more practical metallurgist, will find here material of interest. The illustrations are very carefully drawn and are printed with unusual clearness. A translation of this admirable work into English would supply a deficiency in America and England. H. C. J.

LEHRBUCH DER ELEKTROCHEMIE. VON DR. MAX LEBLANC, Privatdozent an der Universität, Leipzig. With 32 figures in the text. Leipzig: Oskar Leiner, 1896. pp. 226.

An introductory chapter, dealing with the principles and laws underlying the study of electricity, is followed by a brief historical sketch of the development of electrochemistry up to the present. Chapter 3 has to do with Arrhenius' theory of electrolytic dissociation, tracing the rise of this theory also historically. Under wandering velocities of ions, the classic work of Hittorf is brought very prominently to the front; a table of Hittorf's values for the velocities of a number of anions, concluding this subject. Chapter 5 is devoted to the conductivity of electrolytes, treating of the law of Kohlrausch, the determination of dissociation-constants by means of measurements of conductivity, the relation between dissociation-constants and chemical constitution, dielectric constants of solvents and their dissociating power, etc., and is characterized by clearness throughout. Chapter 6 forms nearly half of the book. It treats of electromotive force, including a discussion of the relation between chemical and electrical energy; an account of what is meant by electrolytic solution-pressure, and of its application in the calculation of potential differences; the concentration element, the liquid element, the thermal element, and the chemical element. The

author is in an especially favorable position to deal with polarization, which is the subject of Chapter 7, since much of the work there described is his own. He may, however, find readers who will not entirely agree with him as to the primary decomposition of water in electrolysis. The book concludes with an account of the constant and inconstant primary batteries in common use, and with a brief statement with respect to accumulators.

This work is less complete, in parts, than that of Jahn, (Grundriss der Elektrochemie), but this is somewhat offset by its admirable system, which is, in the main, that adopted by Ostwald, in that part of his Lehrbuch which deals with electrochemistry. Le Blanc expresses his indebtedness to this source, and to Ostwald in person, for invaluable assistance. While there are some omissions to which it is difficult to become reconciled, one is inclined to avoid any unfavorable comment on a piece of work, which, as a whole, has been done so well. H. C. J.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. By CHARLES R. SANGER, A.M., Ph.D., Eliot Professor of Chemistry in Washington University. St. Louis: Published by the Author. 1896. 60 pp.

The experiments here described do not differ markedly from those included in several other compilations. In fact, Professor Sanger says "they are compiled from various sources." The author has, of course, endeavored to select the best from a number of manuals and, no doubt, for the object he has in view, he has succeeded in making a better guide than any of those from which he has drawn. It is intended for students of the Engineering School, and for students of the College who may elect the course.

A SHORT COURSE OF EXPERIMENTS IN GENERAL CHEMISTRY WITH NOTES ON QUALITATIVE ANALYSIS. By CHARLES R. SANGER, A.M., Ph.D., Eliot Professor of Chemistry in Washington University. St. Louis: Published by the Author. 1896. 50 pp.

The author has been worried, as many others have been, by the question "What ought to be done in Chemistry for the medical student?" His state of mind is revealed by the following passage taken from the preface of this little book: "The aim of the course is to teach as much of the theory of Chemistry and to impart as much practical knowledge of qualitative methods as is possible in the limited time (seven months) which can be devoted to it. For this reason no special attempt is made to teach the subject from the purely medical stand-point, for the author believes that a good theoretical and practical foundation is necessary before taking up

the special subject of medical chemistry. In other words this course takes the place, so far as it can, of the more extended collegiate courses in General Chemistry and Qualitative Analysis, which the author hopes to see at some time made a condition of entrance to all medical schools. So long, however, as a medical school is obliged to provide for elementary instruction in chemistry, this should be of such a nature as to impart essential facts through the student's own work and deduction in the laboratory, with as little as possible of book work."

This is sound doctrine. The experiments appear to be well chosen, and the descriptions clear.

THE SCIENTIFIC FOUNDATIONS OF ANALYTICAL CHEMISTRY, TREATED IN AN ELEMENTARY MANNER. By WILHELM OSTWALD, Ph.D. Professor of Chemistry in the University of Leipzig. Translated with the Author's sanction by GEORGE M'GOWAN, Ph.D. Macmillan and Co.: New York and London. pp. 207. Price, $1.60.

Since the original German edition of this work has already received notice in this Journal,[1] it remains but to call attention to the appearance of the English translation. It is stated in the Translator's preface, that "Professor Ostwald has made here and there an emendation upon the original German edition, and has added a section of a chapter upon electro-analysis." In some eight pages the electrolytic deposition of the metals is thus placed with other analytical processes, on a scientific basis.

The work of Dr. M'Gowan deserves high commendation. He has not added to the unfortunate attempts to translate German literally into English, but, without sacrificing the meaning of the original, has prepared, not only a readable, but an attractive book. Indeed, from the point of view of clearness, the English in many places, does not suffer by comparison with the original. The accuracy of the translation is assured by the fact that Professor Ostwald has examined the revised proof-sheets. H. C. J.

A TEXT-BOOK OF GAS MANUFACTURE FOR STUDENTS. By JOHN HORNBY, F. R. C. London: John Bell & Sons. New York: Macmillan & Co., 1896. $1.50. 225 pp.

This book in intended for young men studying gas engineering, and as a text-book for those preparing for the examinations of the City and Guilds of London Institute. It is an excellent book. The chemistry of gas manufacture is clearly and sufficiently treated, yet in a way intelligible to those whose knowledge of chemistry is but slight. The thorough

[1] Vol. 16. 564.

explanation of different methods of manufacture and of mechanical detail make it interesting and valuable to any reader. E. R.

THE ELEMENTS OF CHEMISTRY. By PAUL C. FREER, M.D., Ph.D., University of Michigan. Boston: Allyn and Bacon, 1895. pp. 284.

Prof. Freer's book differs from any of the chemical text-books in use. It treats of the elements hydrogen, oxygen, nitrogen, chlorine and carbon, of water and air, of the oxides of carbon and sulphur, of the oxides and hydroxides of sodium and potassium, of hydrochloric, carbonic, and sulphuric acids, of chlorides of primary and secondary carbonates and sulphates, of ammonia and ammonium salts, of methane and its chlorine substitution-products. This is all. A careful and lucid study of the above with eighty-one laboratory experiments, many of which are quantitative, serves as a basis for an admirably clear and simple treatment of chemical theory.

A student intending from the outset to follow chemistry as a profession would profit greatly by beginning with the study of this book with a good teacher.

The limited amount of time given to chemistry in school or college will, however, prevent the general introduction of a book treating of so few elements aud compounds, and demanding so large a proportion of the time allotted. E. R.

REPERTOIRE DES RÉACTIFS SPÉCIAUX, GÉNÉRALEMENT DÉSIGNÉS SOUS LEURS NOMS D' AUTEURS. FERDINAND JEAN: 17, Faubourg-St-Denis, et G. MERCIER, 158, rue Saint-Jacques. Paris, 1896. 12 mo.

The large number of reactions and tests which have come into use, and are generally referred to, in the literature, by name only, warrants and renders valuable any attempt at such a compilation; but as the authors have, within the space of one hundred pages, collected (in alphabetical order) some four hundred such reactions, principally relating to physiological and pharmaceutical chemistry, it has been scarcely possible to give them in all cases in sufficient detail to be useful. It would have considerably enhanced the value of the book had references been given to the original articles or more extended works. Many common tests have been overlooked. Numerous typographical errors occur, and the quality of the paper is not what is to be desired in a book intended to be handled. M. D. S.